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PHYSICS

A PRECISION METHOD OF MEASURING SMALL CHANGES OF LATTICE SPACINGS OF METAL SINGLE CRYSTALS

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Abstract

A method of studying the progressive crystal lattice changes occurring in a series of alloys or mixed crystals is described. This method compares the Bragg angles of x-ray reflection from a standard crystal with those of the crystal being studied. The important features of the method are simplicity and high accuracy (0.002 percent), which is attained without the use of an accurately calibrated angle scale. The theory of the method is discussed and two examples of experimental data which have been obtained are given.

Introduction

THE study of the crystal lattice of metal single crystals containing small known amounts of impurities in solid solution becomes important in view of the large influences on certain physical properties, which is exerted by very small admixtures of enantiomorphous but soluble metals, such as have been reported by Goetz and Focke[1] for the magnetic susceptibilities of Bi single crystals.

Investigations of this kind require a precise measurement of the Bragg angles of x-ray reflection from various crystal planes in order to determine the mode of change of the crystal lattice as the amount of substance added to the original substance is increased. Since the changes in lattice spacings which are to be expected are a fraction of a percent, it is necessary to have a method of measurement which is accurate to at least 0.01 percent, and if possible to 0.001 percent. Such accuracies of measurement of the Bragg angle are beyond the scope of the usual x-ray crystallographic measurements and have heretofore only been attained by using the Siegbahn method of measurement, whose accuracy depends upon the precision of the angle scale which is used.

The author has devised a comparison method of Bragg angle measurement based upon the Siegbahn method and having the following advantages:

(1) Changes of lattice spacing may be measured to an accuracy of 0.002 percent.

(2) This accuracy is independent of the angle scale used, so a precision angle scale is not necessary.

[1] A. Goetz and A. B. Focke, Phys. Rev. **38**, 1569 (1931); Science **74**, 603 (1931).

(3) Any errors in the Bragg angle measurements which may be introduced by the crystal face being displaced slightly from the axis of rotation is completely compensated for. Such compensation is necessary because many of the crystals to be studied do not have large crystal surfaces of good optical perfection such as are required for the Siegbahn method[2] of adjusting the crystal face in the axis of rotation, and therefore small errors in this adjustment may occur.

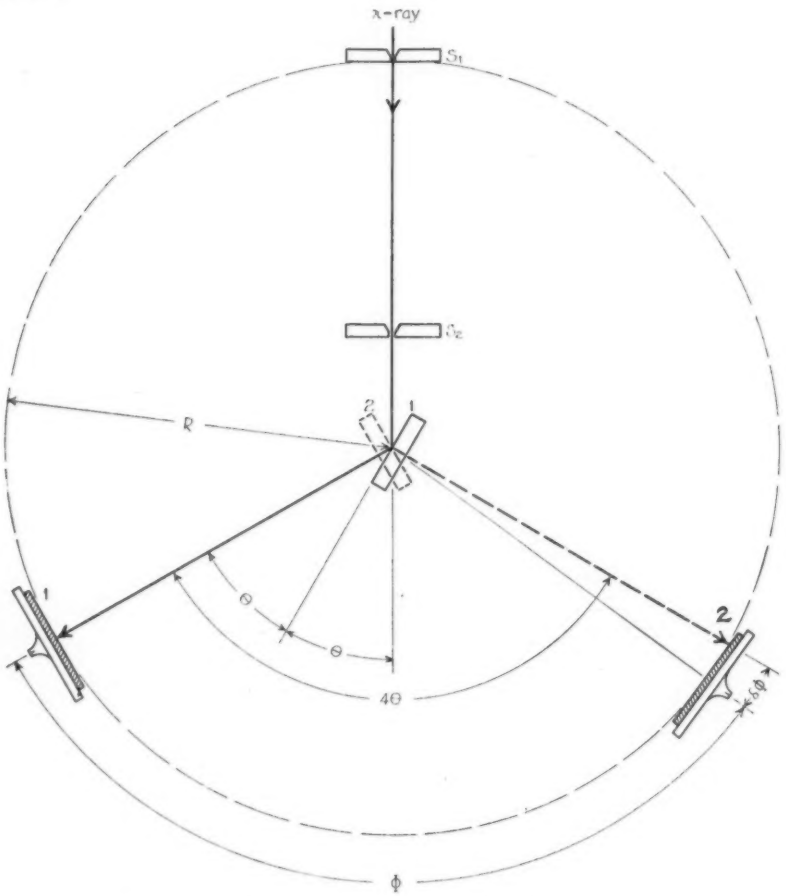

Fig. 1. Siegbahn's method of measuring Bragg angles.

Theory

The theory of this comparison method is as follows. In Fig. 1 is illustrated the Siegbahn method of measuring the Bragg angle. The incident x-ray beam passes through the fine slit S_1 and the wider slit S_2, the two slits being so adjusted that the beam passes through the axis of rotation of the crystal. If a crystal with its reflecting face lying in the axis of rotation is turned to the Bragg angle (position 1), reflection of the x-rays occurs to the photographic

[2] Spektroskopie der Röntgenstrahlen, M. Siegbahn, p. 67.

plate in position 1. If the distance of the slit S_1 from the axis of rotation equals the distance R of the photographic plate from this axis, the Bragg focussing condition is fulfilled and a sharp image of slit S_1 is produced on the plate. The crystal is now turned to position 2 and the photographic plate (which is mounted on an arm whose axis of rotation coincides with that of the crystal) is turned through a measured angle ϕ, and a second reflection is recorded on the plate. If ϕ differs slightly from 4θ, the two images fall in slightly different positions on the plate and their separation L can be accurately measured with a comparator.

$$\begin{aligned} L &= R\delta\phi \\ 4\theta &= \phi + d\phi. \end{aligned} \tag{1}$$

In the author's method, the two crystals which are to be compared are mounted one above the other as is illustrated in Fig. 2. In this way the reflec-

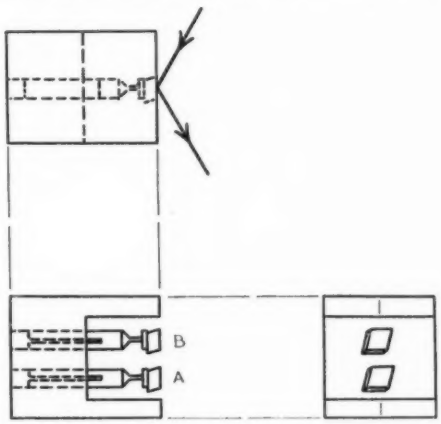

Fig. 2. Double crystal holder. A is the standard crystal and B is the crystal to be compared with A.

tions of x-rays from both crystals are simultaneously recorded in each of the two positions already described. The separation of the two pairs of images is then measured with a comparator giving L_a and L_b.

$$L_a - L_b = R(\delta\phi_a - \delta\phi_b) = 4R\delta\theta \tag{2}$$

where $\delta\theta$ is the difference in the Bragg angle of reflection from the two crystals. It is to be noticed that ϕ has dropped out of consideration and the entire precision rests on the comparator measurements L_a and L_b.

If we take the Bragg equation

$$n\lambda = 2D \sin\theta$$

and differentiate, we get

$$d\theta = -\frac{n\lambda}{2D^2}\frac{1}{\cos\theta}dD.$$

Substituting (2) we get

$$L_a - L_b = -\frac{2R\lambda}{D^2}\frac{n}{\cos\theta}\delta D. \tag{3}$$

Let us assume that the crystals are perfectly aligned with the axis of rotation and that these measurements are made for at least two orders of x-ray reflection from the crystal faces. If the measurements L_a–L_b are plotted against the values of $n/\cos\theta$ the result will give points on a straight line passing through the origin, and the slope of this will be $(2R\lambda/D^2)$ (δD), where δD is the difference in lattice distances for the two crystals respectively.

The way in which a displacement of the crystal face from the axis of rotation will affect the Bragg angle is shown in Fig. 3. The correct position of

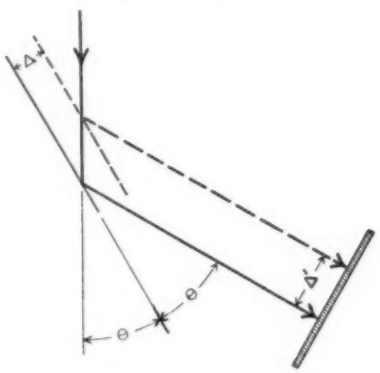

Fig. 3. Error caused in the position of the image on the photographic plate when the crystal face is displaced a distance Δ from the axis of rotation.

the crystal face is shown by the broken line and the actual position displaced a distance Δ normal to this is shown by the solid line. The resulting displacement of the image on the photographic plate is Δ′ which is given by the equation

$$\Delta' = 2\,\Delta\cos\theta.$$

It is clear that when the crystal is turned to give the symmetrical reflection on the other side, the displacement of the other image from the correct position will be symmetrical giving a change in L equal to twice Δ′

$$2\Delta' = 4\Delta\cos\theta.$$

The deviation of L_a–L_b from the correct value is given by

$$2(\Delta_a' - \Delta_b') = 4(\Delta_a - \Delta_b)\cos\theta.$$

In such a case the data when plotted will give the sum of the straight line through the origin already described, and the above cosine curve. The resultant curve will be tangent at the origin to the straight line displaced along the ordinate by an amount $4(\Delta_a - \Delta_b)$. If this quantity is small, the resultant curve will be a straight line within experimental error because the cosine de-

creases only 10 percent at 26 degrees which represents the largest Bragg angles ordinarily involved. If $\Delta_a - \Delta_b$ is large compared to the experimental error of the comparator measurements, the curvature for the best fitting

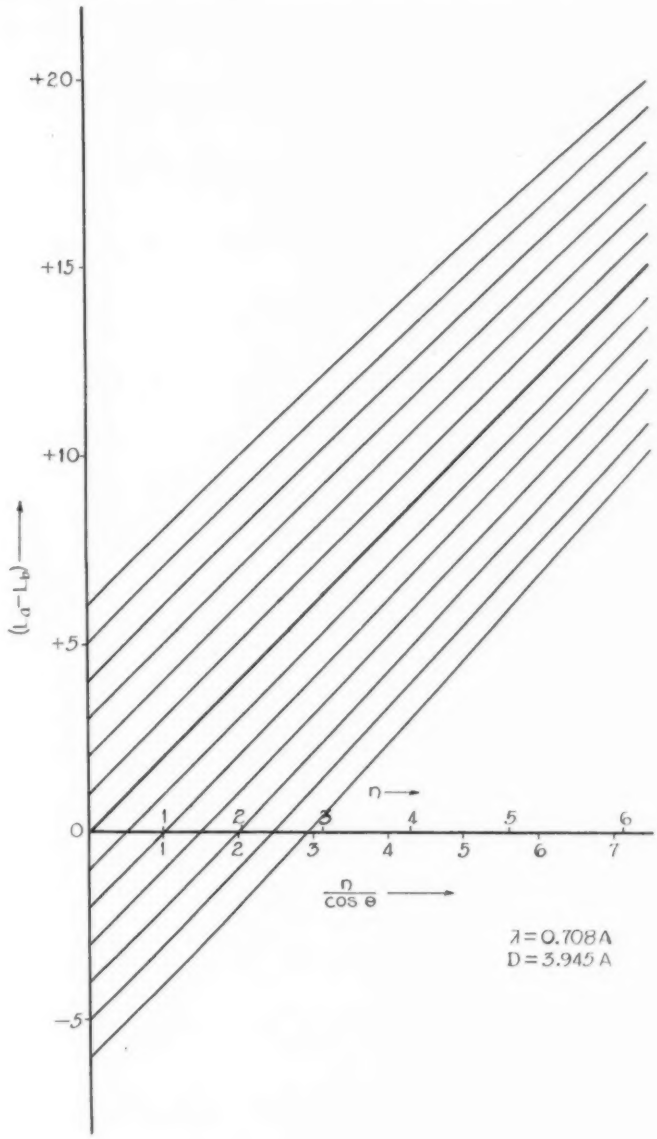

Fig. 4. Theoretical curves for various values of $(\Delta_a - \Delta_b)$ when the ordinate is chosen such that the corrected curve has unit slope.

theoretical curve can readily be computed. Fig. 4 shows the theoretical curves for various values of $\Delta_a - \Delta_b$ when the ordinate is so chosen that the corrected curve has a slope of 45 degrees.

Results

In Figs. 5 and 6 are shown two sets of experimental data[3] obtained from Bi single crystals containing different amounts of Sn, by means of the above described method. Although four orders of reflection were measured, this was

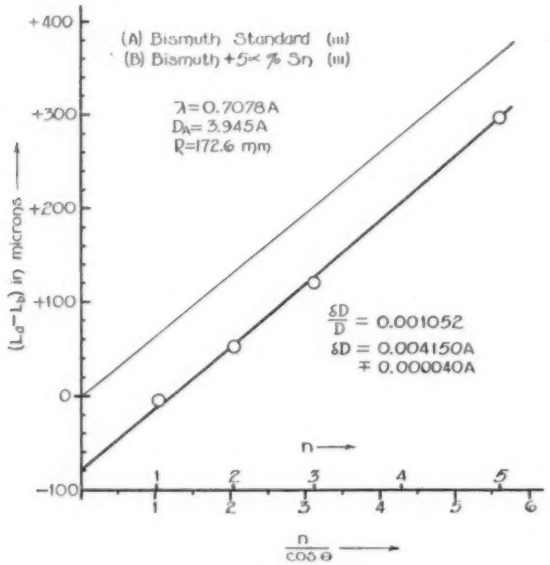

Fig. 5. Experimental data for comparison of Bi with Bi+5α percent Sn. The straight line through the origin is the corrected curve.

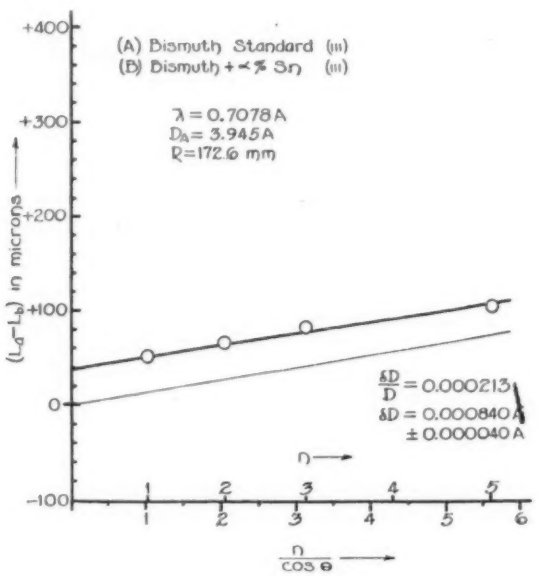

Fig. 6. Experimental data for comparison of Bi with Bi+α percent Sn. The straight line through the origin is the corrected curve.

[3] A discussion of these results will be presented, among others, in a later article.

done to check the accuracy of the method. Only two orders of reflection are necessary and these should be as widely separated as possible. It was found upon repeated comparator measurements of L_a and L_b that the results checked within 5 microns, which represents the uncertainty of the estimation of the center of a line. This value when substituted in Eq. (3) gives an uncertainty of 0.0014 percent D in the value of δD.

The author used a Siegbahn spectrometer for making these measurements.[4] However, as has been pointed out already, just as accurate results could have been obtained by using a much simpler design of instrument. Molybdenum radiation was used for these measurements so it was not necessary to exhaust the apparatus. The slit S_1 was 0.1 mm and the distance R 172.6 mm. For each exposure the crystal holder was turned with a uniform angular velocity from a position 1/2 degree smaller than the Bragg angle to a position 1/2 degree larger than the Bragg angle. This angular velocity was adjusted for each order of x-ray reflection so that the blackening of the image on the photographic plate was of optimum density.

Conclusion

It would be possible to mount as many as five or six small crystals in a suitable holder and measure these simultaneously with the standard crystal. Such a scheme would greatly reduce the labor of studying the progressive crystal structure changes in a series of microalloys or mixed crystals. The error in the Bragg angle caused by the divergence of the incident ray occuring with a long slit is the only limiting factor in such a case. The change in θ which is introduced in the reflected ray when the incident ray makes an angle ϕ with the equatorial plane (perpendicular to the plane of the crystal face) is given by

$$d\theta = \frac{\sin 2\theta}{2} \phi^2.$$

The author wishes to express his indebtedness to Dr. A. Goetz who suggested the development of such a method and to Mr. R. Jacobs who assisted in the experimental work.

[4] Spektroskopie der Röntgenstrahlen, M. Siegbahn, page 64.

AN ATTEMPT TO ACTIVATE ADSORBED MERCURY ATOMS BY ULTRAVIOLET LIGHT*

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IT HAS been rather well established by Professor H. S. Taylor and his co-workers, as well as by other investigators that the surfaces of solids, used to catalyse gas reactions, exhibit activities in varying degree. These investigators attribute the variation in the activity of catalysts to the existence on the surface of the catalyst of extra-lattice atoms of different degrees of saturation. The most active parts of the surface are considered to be those which have the greatest number of atoms in this partially unsaturated extra-lattice condition. It is known for example that an active catalyst may be partially poisoned so that it no longer will be active in certain reactions yet it will continue to be effective in reactions which may be carried out by the aid of less efficient catalysts. In such cases it is considered likely that the most highly unsaturated atoms are the first to adsorb the molecules of the poisoning agent. Successive additions of the catalyst poison render inactive the less and less active areas of the surface. It has even been suggested that the most active catalyst atoms on the surface are approaching the condition of gas atoms.

The exact mechanism by which the surface atoms of catalysts activate molecules and thus cause reaction is not entirely clear. If these surface atoms really approach gas atoms then it is possible that they may pick up radiation in a manner similar to that of mercury vapor and thus activate molecules so that chemical reactions follow. Taylor and Hill[1] have shown that atoms of mercury vapor in the $^1S_0$ state which have absorbed light of wave-length 2537A and become Hg $^3P_1$, are capable of activating a mixture of hydrogen and ethylene so that one or more reactions follow. In the experiments here reported an attempt was made catalytically to activate mercury atoms, which had been adsorbed on an active copper catalyst, by illuminating with the light from a mercury arc lamp.

Experimental Part

An active copper catalyst was prepared by adsorbing cupric ammonio ions on silica gel.[2] This impregnated silica gel was then dried and the copper salt reduced to metallic copper by passing hydrogen over the gel at about 200°. This produces a very uniform black deposit of Cu on the surface of the silica

* This research was made possible by a grant from the Research fund of the Graduate School of the University of Minnesota.

[1] H. S. Taylor and D. G. Hill, J. Am. Chem. Soc. **51**, 2922–36 (1929).

[2] Grant W. Smith and L. H. Reyerson, J. Am. Chem. Soc. **52**, 2584 (1930).

gel. The silica gel was felt to be desirable as a support material because it offered a large irregular surface on which large numbers of extra-lattice atoms could exist. Furthermore the silica gel, being almost pure SiO_2, would not of itself interfere with the passage of the ultraviolet light through the catalyst. The first experiments were carried out by passing a mixture containing purified ethylene and hydrogen over the catalyst contained in a quartz tube. Concentrations of ethylene were varied from 15 to 30 percent in the various runs and the temperature of the catalyst was maintained at 85°. Samples of the gas mixture, taken before and after passing the catalyst, were analysed in the usual way in an Orsat-Lunge gas analysis apparatus. The freshly prepared or re-activated catalyst was found to be very effective in the hydrogenation of ethylene at reasonable rates of gas flow. The catalysts lost activity gradually with use but they could always be reactivated by allowing them to stand for several hours in an atmosphere of hydrogen. A catalyst

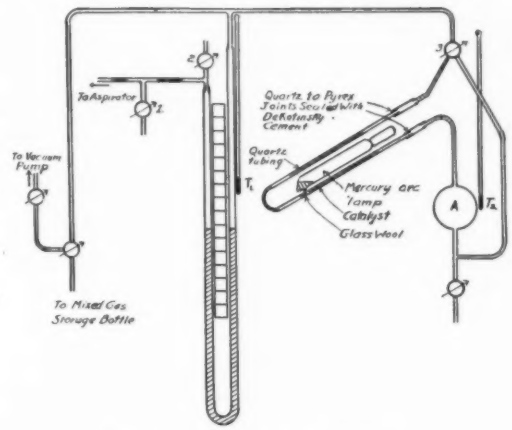

Fig. 1. Diagram of apparatus.

whose activity was determined by analysis was illuminated by a mercury arc lamp for about an hour during a regular run. Analysis of samples of gas taken after passing the catalyst during the illumination showed no increased catalytic activity as a result. The catalyst was then poisoned completely for the hydrogen-ethylene reaction by adsorbing mercury atoms on the active copper surface. The poisoned catalyst was then subjected to the ultraviolet light during the passage of the gas mixture but no hydrogenation could be detected by the methods of analysis used.

A completely closed system was then constructed so that any reaction of the gases could be followed by pressure changes in the system. The apparatus is illustrated in Fig. 1. The gas mixture could be circulated past the catalyst by alternately raising and lowering the mercury in the manometer. By properly setting valve No. 3 and lowering the height of the mercury in the right side of the manometer the gases could be drawn through the catalyst from bulb A. By changing the setting of valve No. 3, so that it connected the manometer directly to A, the gases could be returned to A by allowing air to enter the

left side of the manometer thus forcing the mercury up in the right side, and displacing the gas into *A*. This constitutes one circulating pump action. These actions were spaced at regular intervals between manometer readings. The mercury lamp radiated enough heat so that the catalyst tube had to be cooled by running tap water over it from twenty small jets. The pressure of the mercury vapor in the lamp was kept low by immersing the mercury well of the lamp in running water. With fresh catalyst in the catalyst tube and no illumination the change in the manometer readings showed that the catalyst was very active. The system was then evacuated and the catalyst poisoned by distilling mercury vapor through it. Visible mercury on the catalyst was removed by gentle heating. The process of poisoning had to be repeated twice before the catalyst was found to be inactive.

A mixture of hydrogen and ethylene containing fifty percent ethylene was then circulated past the poisoned catalyst for a period of 28 hours. The catalyst was maintained at about 3° during this run. The mercury lamp was turned on for three hours of this period. No significant pressure changes were observed during the complete run. The catalyst was then removed from the system and a few drops of mercury introduced into the catalyst tube. Wet steam was passed over the tube instead of the cooling water so that the fresh gas mixture which was introduced would be saturated with Hg vapor at 99°C. Gas circulation was started and manometer readings taken. Upon illumination for a period of 1–1/2 hours the pressure in the system fell regularily. This was repeated the next day with the same result. In each case the calculated volume of the system diminished by about 4 cc during 1–1/2 hours of illumination. With no illumination there was no pressure change. The catalyst tube was therefore getting sufficient ultraviolet light to activate the mercury vapor. The work of Taylor and Hill is thus confirmed insofar as the action of the activated mercury atoms on the hydrogen-ethylene mixture is concerned.

Conclusion

Mercury atoms adsorbed on catalytically active extra-lattice copper atoms are not activated by the light from a mercury lamp sufficiently to cause a reaction to occur between hydrogen and ethylene. Hg in the vapor state under similar conditions does cause such an action to take place.

The author wishes to thank Mr. Standish Miller who assisted in this work under the grant from the Graduate School.

POTENTIAL DISTRIBUTION, RADIATION AND ELECTRICAL CONDUCTION IN PAPER

By Edward B. Baker and Robert F. James

The Detroit Edison Company

(Received December 11, 1931)

Abstract

The nature of electrical conduction in paper is discussed, particularly with regard to the formation of potential discontinuities. Experiments are described which indicate the formation of soft x-rays in paper insulated cables under voltage. Methods of measurement of potential distribution in paper insulation are given, together with preliminary results, which show large electrode drops under certain conditions. The relation of these experiments to those of Reboul and Bodin is pointed out.

Introduction

THE widespread use of oil-impregnated paper as an insulator for high-tension cables has initiated a rather intensive program of research in the last few years, with the object of understanding and improving this insulation. This complex and interesting problem is attracting the attention of increasing numbers of physicists. A number of powerful theoretical and experimental tools are now available for an attack on this problem, and that of the nature of dielectric and semi-conducting media in general.

It is the primary purpose of this article to describe methods of measurement of potential distribution in paper, to present some preliminary results, and to relate these results to the interesting experiments of Reboul and Bodin,[1] at the same time indicating their possible practical importance. In addition it is thought highly desirable to organize briefly some of the possible means of conduction in paper, and to suggest means of studying them quantitatively.

It seems to the present authors that a fundamental study of conduction in oil-impregnated paper should begin with the study of paper alone. It is believed that in the presence of relatively small amounts of moisture the anomalous electrical behavior of oil-impregnated paper is contributed predominately by the paper alone. Of course, under certain conditions of temperature and frequency, where dipole loss in the oil is high, or if the voltage is high enough for cumulative ionization, this may not be true. If the paper were pure it undoubtedly would not be the case. For this reason, until purer paper is used the study of paper alone should be a major part of the problem.

Pure cellulose is known[2] to be a very perfect insulator, practically all of

[1] G. Reboul, Jour. de Phys. et le Radium [6] **7**, 275 (1926): Comptes Rendus **171**, 1052 (1920); **172**, 210 (1921); **173**, 1162 (1921); **174**, 1451 (1922); **180**, 916 (1925); **180**, 1735 (1925), and R.G.E. Sept. 24, 1921, p. 393.

G. Reboul and P. Blet, Comptes Rendus **176**, 86 (1923).

E. Bodin, Comptes Rendus **180**, 1731 (1925), Ann. de Physique [10] **7–8** (1927).

G. Reboul, Jour. de Physique **3**, 86 (1931).

[2] E. J. Murphy and A. C. Walker, Jour. Phys. Chem. **32**, 1761 (1928).

its conduction being due to impurities. Kraft paper, as usually used in cable insulation, has a high resin and ash content. Little is known of the effect of resins upon electrical properties, though they are thought rather essential for mechanical strength. It would seem *a priori* that they might contribute slightly to a.c. loss and perhaps somewhat to d.c. conduction but their effect should be small. Some work on this point is desirable. The ash consists[3] partly of inert material such as silica, but principally of inorganic salts, whose importance in conduction in the presence of moisture may be easily realized.

It is rather generally believed that moisture may be held in paper in several different ways, and that in the process of drying it is removed in the following order: (1) held mechanically; (2) absorbed in capillaries; (3) adsorbed on fiber surfaces; (4) water of hydration of cellulose; (5) water actually composing cellulose. Naturally the temperature and other conditions of drying determine to what extent it is removed. Measurements[4] of adsorption isotherms of water on charcoal seem to indicate that this removal of water proceeds in observable steps if the temperature is not too high. Work of this sort on paper under carefully controlled conditions, as well as careful calorimetric studies of the same problem, hold a great deal of promise in determining quantitatively the distribution of moisture among these forms of combination, as well as such things as pore area and heats of adsorption. It must be emphasized that the distribution of moisture among these forms is undoubtedly quite temperature-sensitive. It is of the utmost importance to have more quantitative information about these things because they determine the nature of the medium in which the ions move. A possible effect of the presence of resins is to change this distribution, and experiments should be performed on good ashless filter paper from which resins have been removed.

It seems plausible to assume that paper, dried so that all the moisture present is held in "true" chemical combination (including water of hydration), could furnish no medium for the transportation of ions, that conduction and losses should then be negligible, and that the inorganic salts would simply contribute a small amount to the real dielectric constant.

If, in addition, adsorbed water is present, several new effects should be observed. The inorganic salts, if not already ionized by adsorption on the surface of the cellulose, should be at least partly dissociated in the presence of adsorbed water. These, if free to move at all, will contribute in a very special manner to d.c. conduction due to their greatly decreased mobility (adsorption forces), i.e., they will contribute to absorption current but will affect only the long time potential distribution. They will contribute to a.c. loss by the mechanisms described by Murphy, Falkenhagen[5] and others, wherein the

[3] A. C. Walker in a paper presented before the Insulation Committee of The National Research Council.

[4] Allmand and Burrage, Proc. Royal Soc. **A130,** 610 (1931); Allmand and Puttick, Proc. Royal Soc. **A130,** 197 (1930); Burrage, J. Phys. Chem. **34,** 2202 (1930).

[5] H. Falkenhagen, Rev. Mod. Phys. **3,** 412 (1931); E. J. Murphy and A. C. Walker, reference 2.

movement of ions in an alternating field is accompanied by a frictional resistance, in this case largely caused by forces of adsorption. Much quantitative information of extreme value bearing on this point could be obtained by investigation of the power factor-frequency-temperature surface under sufficiently controlled conditions. It would be necessary to use very pure paper, containing known amounts of known inorganic salts and known quantities of water (controlled humidity).

As the amount of water present is increased, so that adsorption forces become less prominent in determining ionic mobilities, then short time effects in d.c. conduction and Joule loss by increased currents of faster ions become important. These effects should show decisively in power-factor-frequency-measurements, and a definite correlation should exist between these measurements and the adsorption isotherms. Another factor, electrode polarization, enters at this point, and in some cases may cause vital anomalies. Of course, in some dielectrics the mysterious "dielectric polarization" potential discontinuities[6] may appear, an essentially different phenomena, but we believe that the balance of evidence that we have obtained so far discredits their presence in paper. We have observed potential discontinuities, but we believe them to be electrode polarizations caused by fast moving ions which are unable to discharge at the electrodes as rapidly as they are carrried there.

If still more moisture is permitted to be present its distribution on the paper may well be affected by the presence of a field (Evershed effect), and the situation becomes more complex and difficult to control. It must be cautioned that when large amounts of moisture are present the electrodes take a more prominent part in the electrolysis, and results will depend upon the material composing them. For example, with ordinary cable paper containing a fairly large amount of moisture, we have found that continued application of direct potential eats away one of the nickel electrodes and carries the nickel to the other, coloring the paper. Also, if high voltages are used, or if large gradients occur in the dielectric, the presence of air or other gas will play a more prominent part than simply furnishing a contribution to the dielectric constant.

If there is really no conduction in the cellulose proper then there will be no Maxwellian loss. If oil is added, however, its separate losses should be incorporated with those of the moisture in the paper with Maxwell's idea in mind. It must be remembered, however, that moisture adsorbed in a thin film may have a radically different dielectric constant from that in bulk.

Measurements of potential distribution and its variation with time will perhaps furnish quantitative values of ionic mobilities and absorption forces by the application of a suitable modification of Mie's[7] theory, in which "plating out" action is also taken into account.

In view of the fact that it is possible to control all of the variables that enter into work with paper alone, this study may be put up on a very sound basis. Of course, the very obvious practical solution is to remove inorganic

[6] A. Joffé, "Physics of Crystals", McGraw Hill Publishing Company, (1928).

[7] G. Mie, Ann. d. Physik **13** (5) 857 (1904).

salts from the paper, but the problem still remains because of the cost of doing this completely. We have outlined a very ambitious program—far too ambitious for one laboratory to complete, and we hope that the problem will be attacked by others from the point of view we have indicated.

X-RAYS FROM CABLES

The study of potential distribution in impregnated cable paper was initiated in this laboratory in connection with work on the deterioration of high tension cables with use; this work has heretofore largely been concentrated upon the chemical effects of corona discharge and electron bombardment, phenomena thought to be similar to those occurring in voids in cable insula-

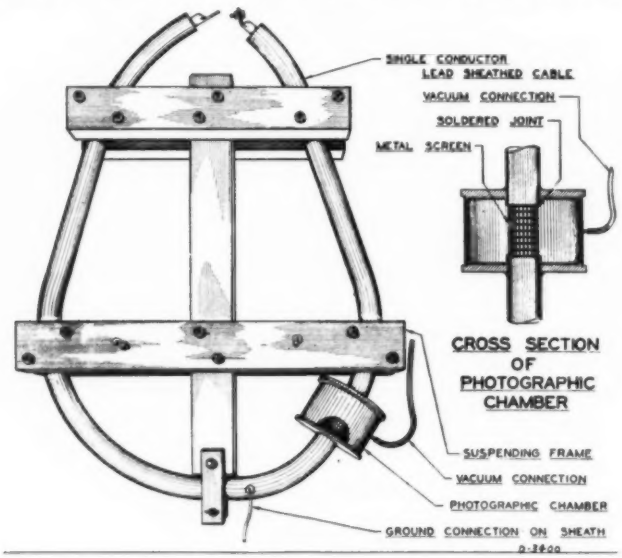

Fig. 1. Diagram of experimental arrangement for demonstrating the production of x-rays from cables. No current is passed through the conductor.

tors. James[8] has suggested that if a gaseous discharge occurs in a void ultraviolet light will be produced, and if the walls of the void are bombarded by electrons soft x-rays may result. Both of these radiations are notorious for their chemical activity and no doubt contribute to deterioration of cable insulation. To our knowledge no critical experiment has yet been performed which could decide whether, in bombardment of insulation by electrons, it is the electrons or the radiation produced which cause the chemical reaction, or in the case of irradiation by x-rays, whether it is the radiation itself or the secondary electrons that are responsible. It is perhaps a meaningless question, in that perhaps it is only necessary to have the required amount of energy present, be it radiant energy or kinetic energy of electrons.

X-radiation has actually been observed in cables by one of the authors. As shown in Fig. 1, a section of the lead sheath was replaced by a copper

[8] Association of Edison Illuminating Companies, 1930 Annual Report. (Printed but not published.)

screen and a photographic film was wrapped loosely around it. Impressions such as pictured in Figs. 2 and 3 were obtained after long exposure. The pressure was partly reduced to diminish the absorption of the soft x-rays in air, although by longer exposure the same effect could be observed at atmospheric pressure. The film was enclosed in thin rubber in each case to eliminate the spurious effects of evolved gas or charged particles. The radiation comes from the surface of the exposed paper between the wires composing the screen. As the distance of the film from the screen is increased the impression becomes more diffuse and, of course, less intense. Films even at a distance of one or two centimeters, while they do not indicate a shadow of the screen, still show effects of exposure to radiation, showing that the explanation does not lie in the possibility that the slightly irregular equipotential surfaces existing just outside of the screen might set up currents in the plane of the film sufficient

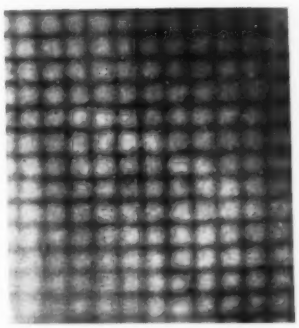

Fig. 2. Shadowgram of the copper screen made on extra fast x-ray film. Exposed for 10 hours at 30 cm pressure and 14 kv.

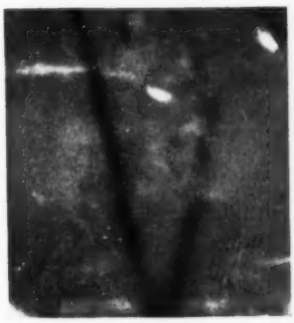

Fig. 3. Shadowgram of narrow strips of lead foil pasted to outside of envelope. Made on extra fast x-ray film exposed for 18 hours at 20 cm pressure and 14 kv.

to cause the observed pattern. The potential applied (14 kv) was not sufficient to set up corona around the cable, particularly since the sheath was at ground potential.

It follows that soft x-radiation was present and that that part observed came from the outer surface of the paper, or just beneath it, since the pattern became diffuse so rapidly with distance, and since soft x-rays are so readily absorbed in impregnated paper. If we assume a logarithmic distribution of potential in the cable it seems highly improbable that these x-rays could be produced by a gas discharge in a void (ordinary "ionization"), since, at the potential used (14 kv) and the pressure existing in the interior (approximately 30 cm), the free path of an electron could very rarely be long enough to allow it to attain an energy of several hundred volts without collision, which would be necessary for the production of x-radiation of this penetrability. This puzzling situation is clarified by comparison with the remarkable experiments of Reboul and Bodin,[1] and sufficient explanation would be forthcoming if a potential discontinuity existed immediately under the screen, over

a distance less than the free path of an electron or ion in the insulation. Reboul and Bodin have shown that such large potential drops exist in compressed tablets of some inorganic salts, and that they are invariably a necessary condition for the formation of the soft x-rays they have observed coming from these tablets. Conduction in such salt tablets is in a number of respects analogous to that in paper insulation, with the exception that the ions are furnished by the salt itself. They found that the production of radiation (10 to 300A for applied potentials of up to 2000 v) is very intimately connected with the dielectric absorption of the tablet. It would appear that much is to be gained by an even more extended investigation of the electrical properties of these "semi-conductors". They are easier to control and work with than very good insulators and yet are very similar to them.

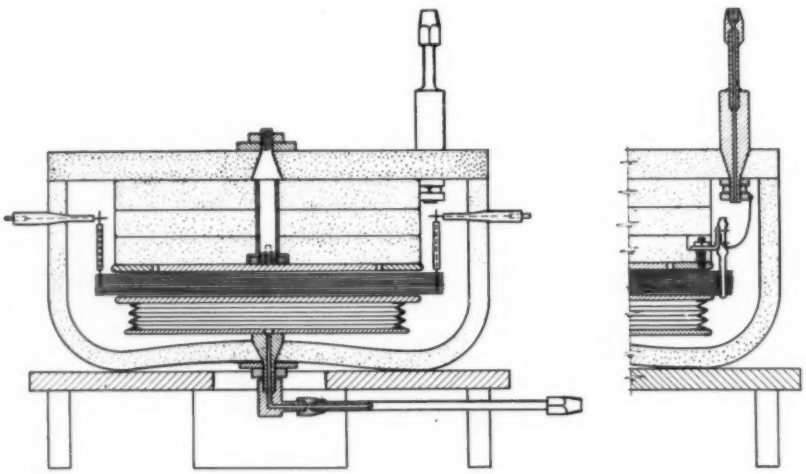

Fig. 4. The flat-plate condenser used for measurements of potential distribution.

Potential Distribution in Paper

We shall present briefly the methods we have found satisfactory for a.c. and d.c. measurements in impregnated paper. The cell used is illustrated in Fig. 4. The Pyrex glass jar has eight quartz tubes containing leads to probes sealed in with litharge and glycerine covered with glyptal lacquer. The upper electrode and its guard ring are fastened on Pyrex disks supported from the cover, which is sealed on with glyptal. The three ground joints which are of Invar having the same coefficient of expansion as Pyrex are bolted in and sealed with glyptal. The lower electrode is soldered to a metal bellows so that any pressure may be applied to the paper. By adjusting the difference in gas pressure between the bellows and the cell proper the desired mechanical pressure may be applied to the paper. The paper may be dried and impregnated in position without exposure to the atmosphere by introducing previously dried and de-gassed oil from an auxiliary apparatus. The guard ring is only used in total current or power factor measurements, being of no use in potential distribution measurements. Such a cell may be heated to 125°C or higher,

and with proper care will maintain a pressure of 1 mm. The type of probe found to be most satisfactory was a 1.5 cm mesh of No. 40 B. and S. bare copper wire. The use of probes is, of course, always open to question since it is very difficult to estimate the magnitude of their disturbing influences. This may be done roughly in certain cases, however.

Direct Potential Measurements

A null method was chosen to measure the probe potentials, as illustrated in Fig. 5. The source of potential is a bank of storage "B" batteries, with an

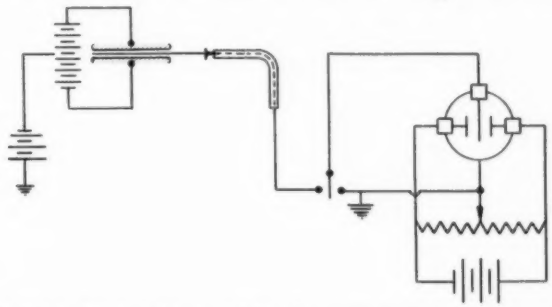

Fig. 5. Wiring diagram of apparatus used for d.c. measurements of potential distribution.

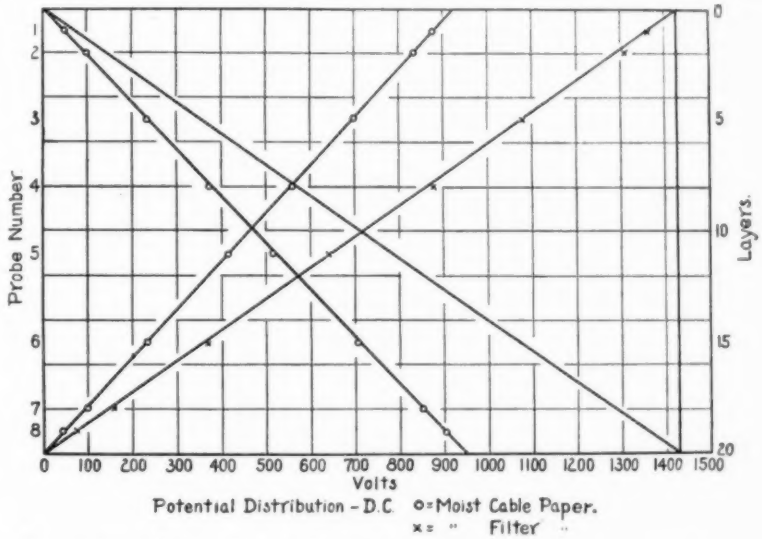

Fig. 6. Direct potential distribution in paper exposed to the atmosphere. Applied potential in each case is 1440 V.

auxiliary battery arranged so that steps of 2 volts may be obtained. The probe to be investigated is connected to a gold leaf suspended between two plates as shown. The central tap of the battery charging the plates is grounded by means of a potentiometer, which also serves to set the instrument to zero. The position of the ground on the main batteries is then varied until balance is attained. The electroscope is thus used as a null voltmeter, and the only current drawn from the probe is that used to charge the leaf and the lead to

it. Since the total current through the cell may be as low as 10^{-10} amperes, the permissible current to be drawn from the probe without disturbing its potential is perhaps 10^{-13} or 10^{-14} amperes. The new General Electric FP-54 was found to be unsuitable for this purpose, though very useful for measureing the total current through the cell.

The results for cable paper (about 1 percent ash) exposed to the atmosphere, and thus containing approximately six percent moisture, are shown in Fig. 6 as circles. The two sets of points correspond to reversed polarities, and serve as checks on the method of measurement. A large drop occurs at the anode similar to that observed by Murphy[2] in cotton fibers. Included in Fig. 6 as crosses are the results on an ashless filter paper, also exposed to the atmosphere. No electrode drop occurs, consistent with the discussion above. Further work will, of course, require more controlled conditions, but these preliminary results indicate that the method of measurement is satisfactory.

Alternating Potential Measurements

The apparatus used for alternating potential distribution is shown diagrammatically in Fig. 7. The delta formed by the potentiometers R_1, R_2 and

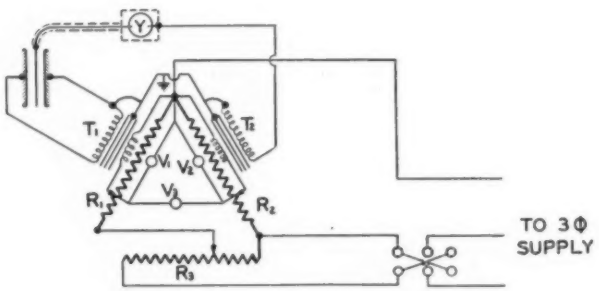

Fig. 7. Wiring diagram of apparatus used for a.c. measurements of potential distribution.

R_3 is connected to a three phase, sine wave, 120 volt generator as indicated. That part of the potentiometer R_1 spanned by the voltmeter V_1 supplies the primary of a step-up transformer T_1 having the ratio 40:1. The secondary potential is applied to the cell. A similar transformer supplies a voltage which is adjusted to that of the probe by means of the null instrument, in this case a vacuum tube voltmeter enclosed in a shield connected to the transformer. A shielded cable is connected to the probe.

Balance is obtained by varying the magnitude of the primary voltage V_2 by means of R_2, and its phase by means of R_3 and the reversing switch, until a minimum voltage is indicated by the null instrument. If this minimum is not zero it indicates the presence of other frequencies. The potentiometer R_1 must be adjusted simultaneously to maintain constant the voltage applied to the cell V_1. The readings V_1, V_2 and V_3 enable the magnitude and phase of the probe voltage to be calculated. It has usually been found that phase displacements are zero within experimental error, and therefore the results may be plotted in two dimensions.

Fig. 8 shows the results on moist cable paper. The points labeled "single probe observed" are measured values obtained by moving a single probe to the desired positions, and those labeled "single probe calculated" are computed from measured capacities assuming a perfect dielectric; the presence of the single probe is thus not sufficient to account for the observed electrode

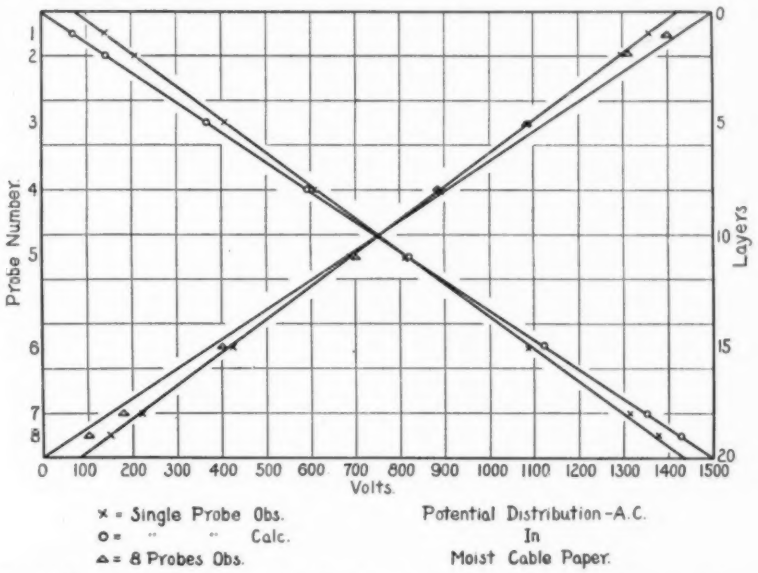
Probe Number
Layers
Volts
0 100 200 300 400 500 600 700 800 900 1000 1100 1200 1300 1400 1500
1 2 3 4 5 6 7 8
0 5 10 15 20
× = Single Probe Obs.
o = " " Calc.
△ = 8 Probes Obs.
Potential Distribution - A.C.
In
Moist Cable Paper.

Fig. 8. Alternating potential distribution in paper exposed to the atmosphere. Applied potential 1500 V.

drops, at least as far as its capacity effect is concerned. With eight probes present the measured values are drawn closer to the lines from corner to corner, particularly the values near the electrodes, as might be expected, since the probes nearest the plates have the highest plate-to-probe capacity. The method used with a.c. is not as satisfactory as might be desired, since the presence of the probes does have a disturbing effect. The relative importance of this effect naturally diminishes as the power factor of the dielectric is increased, or the number of probes present is diminished, but a fixed limitation exists.

DIELECTRIC LOSS AND RELAXATION TIME IN ROSIN

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Abstract

The power factor, dielectric loss and capacitance at 60 cycles of abietic acid have been measured over the temperature range 20° to 100°C. Short time charge and discharge curves, beginning 0.001 sec. after the application or removal of voltage, taken with the amplifier oscillograph, have permitted direct measurement of the relaxation time over the same temperature range. It is shown in general that there are two principal components of the discharge curve which lead to two types of relaxation time, one being the principal factor in the dielectric loss at low temperatures, and the other at high temperatures. The discharge curves have been used for an analysis of the alternating current behavior following the method of von Schweidler. There is uniform agreement between measured and computed loss. With increasing temperature the dielectric constant rises from about 2.6 to 2.8 within the temperature interval 20° to 50°C, the maximum rate of rise being at about 30°, at which temperature the maximum of power factor is also observed. The results are discussed in the light of dielectric absorption in the Maxwell sense and of Debye's theory of polar molecules. The conclusion is reached that alternating current measurements at 60 cycles do not offer a promising method of distinguishing between the two theories, since the same behavior is predicted by each.

Introduction

MANY liquid and solid dielectrics under low frequency alternating potential difference have a minimum of power factor, or phase difference within the temperature range 10–50°C. In many cases (e.g., rosin and rosin-oil mixtures) the rise in power factor toward lower temperatures has been shown to pass through a maximum, with a corresponding decrease in the value of the dielectric constant. This similarity of behavior to that predicated by the Debye theory for polar liquids and solids in much higher frequency ranges has led to the suggestion,[1,2] that the behavior of the oils and rosins at low frequencies (60–500 cycles) is also attributable to polar molecular orientation. Among others Gemant and Bormann[3] have recently presented evidence against this view and attribute the behavior in question to inhomogeneity of the mixture, and consequent residual charge phenomena. It is well known that Maxwell's theory of dielectric absorption or residual charge, extended to the alternating case accounts for a similar type of variation of power factor. The observations on abietic acid, a pure commercial rosin, reported in this paper, appear to have a bearing on this question.

[1] Kitchin and Müller, Phys. Rev. **32**, 979 (1928).
[2] Kirsch and Riebel, Archiv für Elek. **24**, 553 (1930).
[3] Bormann and Gemant, Wiss, Veroff. dem Siemens-Konzern **10**, 119 (1931).

The Experiments

Abietic acid ($C_{20}H_{30}O_2$) is solid and brittle at ordinary temperatures, passing slowly with increasing temperatures through stages of slowly decreasing viscosity to a free liquid condition at about 120°C. The samples here studied were melted in a brass cylindrical tank, into which was immersed the measuring condenser, consisting of three parallel brass plates, the middle, high voltage plate being separated from each of the two low voltage plates by 2.6 mm. The latter were provided with guard rings and their outer faces and all connections carefully screened against external electrostatic influence. The total area of plates was 737 cm², and the capacitance in air 243 mmf. The tank was placed in a constant temperature oil bath, with sealed cover from which the condenser was suspended, and in which the pressure could be reduced to 0.5 mm for drying or other purposes. The quantities measured were the time variation of the charge and discharge currents at 1500 volts continuous potential, and the capacitance, dielectric loss, and power factor at 1500 volts effective 60 cycle alternating potential. The alternating measurements were made with a high sensitivity Schering bridge reading power factor to an accuracy of ± 0.000005. Readings were taken over the temperature range 20°–135°C. The continuous current readings were taken with a General Electric electromagnetic oscillograph in conjunction with 3-stage vacuum tube amplifier,[4] giving 1 mm deflection on the photographic record per 4×10^{-8} amps. in the test condenser circuit.

Fig. 1 shows three pairs of typical charge and discharge records. On first closing the circuit for either charge or discharge the instrument is connected at greatly reduced sensitivity by means of a rapid action switch. The initial low peak on the records indicates this brief interval, during which the circuit transient disappears. The remainder of the record is the charge or discharge (absorption) current of the dielectric. As indicated these records permit the reading of these currents from 0.001 sec. following the application of potential difference or of short circuit. The empirical equations of these curves may readily be obtained by graphical analysis, and so also the relaxation time, as the interval within which the discharge current falls to $1/e$ of its initial value. Some of the curves, conforming to those found for many other types of complex insulating materials, are approximately represented by a single term of the type $i = I_0 t^{-n}$ during the early portion and by another similar term for the later portion. In general, however, it is more satisfactory to write the equation as a series of negative exponentials, i.e., of the type $i_n = \beta_n e^{-\alpha_n t}$. Such terms have finite values for $t = 0$, and in other ways are more satisfactory for discussion and analysis. Over many samples of different materials we[5] have found that three such terms are always sufficient to represent closely the curve, both graphically and in computation, for intervals up to 0.04 sec., which is well beyond that involved in the use of these d.c. curves for the predetermination of a.c. behavior. A family of charge and discharge curves of

[4] Waldorf, Trans. A.I.E.E. **47**, 1418 (1928).

[5] Whitehead and Baños, Winter Convention 1932, A.I.E.E.

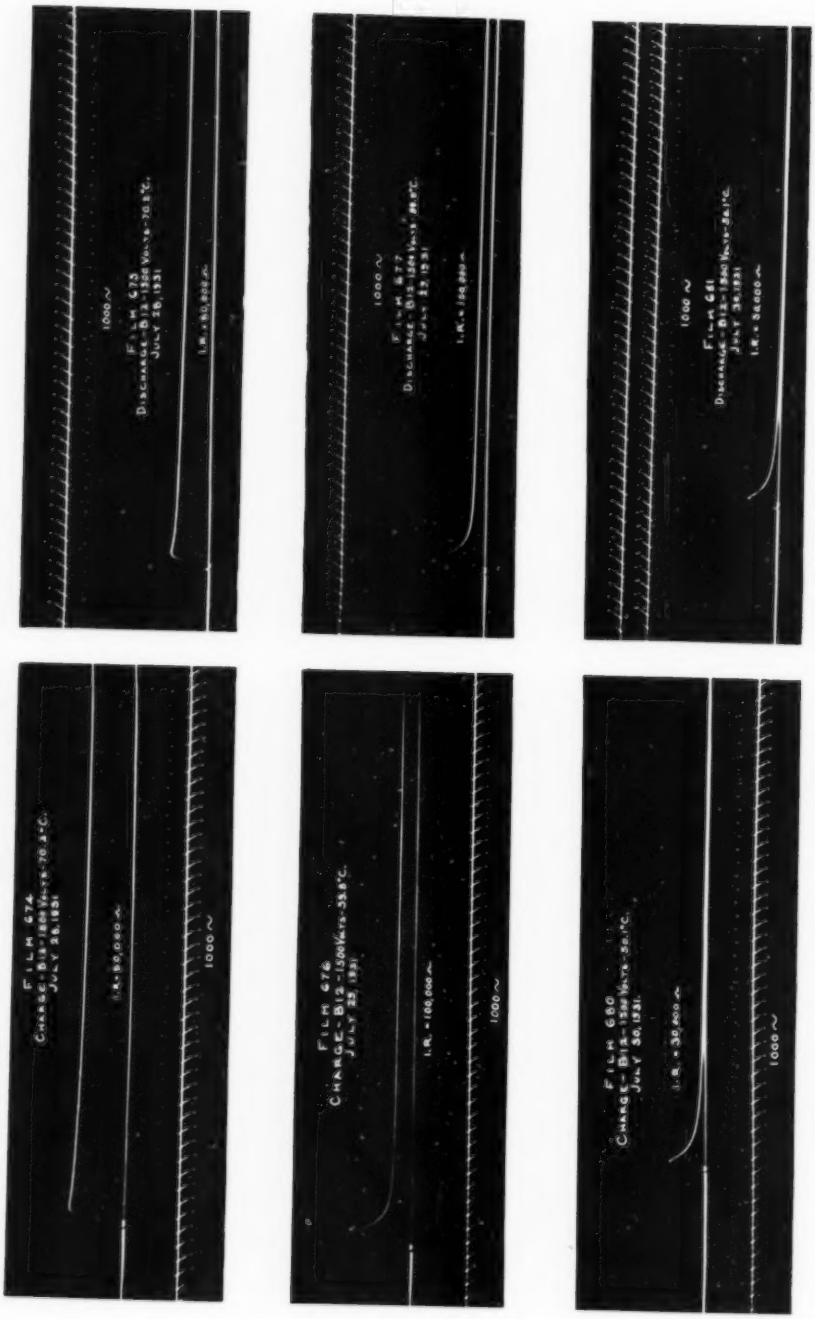

FILM 673
DISCHARGE - B12 -1500 VOLTS - 70.8°C.
JULY 29, 1931
I.R. = 80,000 Ω
1000 ~
FILM 677
DISCHARGE - B12 -1504 VOLTS - 28.8°C.
JULY 29, 1931
I.R. = 160,000 Ω
1000 ~
FILM 681
DISCHARGE - B12 - 1500 VOLTS - 2.1°C.
JULY 30, 1931
I.R. = 24,000 Ω
1000 ~
FILM 674
CHARGE - B12 - 1500 VOLTS - 70.8°C.
JULY 29, 1931
I.R. = 80,000 Ω
1000 ~
FILM 676
CHARGE - B12 - 1500 VOLTS - 33.8°C.
JULY 29, 1931
I.R. = 160,000 Ω
1000 ~
FILM 680
CHARGE - B12 - 1500 VOLTS - 2.1°C.
JULY 30, 1931
I.R. = 36,000 Ω
1000 ~

Fig. 1.

abietic acid over the temperature range 50° to 80° is shown in Fig. 2. The equations of the discharge curves in Fig. 2, are:

$$\begin{aligned}
50.1°\text{C}\, i(t) &= (0.41e^{-107t} + 2.40e^{-628t} + 4.30e^{-2425t}) \times 10^{-6} \text{ amp.} \\
59.8°\text{C}\, i(t) &= (0.32e^{-6.8t} + 2.33e^{-975t} + 5.00e^{-2820t}) \times 10^{-6} \text{ amp.} \qquad (1) \\
70.2°\text{C}\, i(t) &= (1.01e^{-8.6t} + 0.33e^{-663t} + \cdots) \times 10^{-6} \text{ amp.} \\
80.1°\text{C}\, i(t) &= (2.32e^{-10.8t} + 0.59e^{-394t} + 1.81e^{-2730t}) \times 10^{-6} \text{ amp.}
\end{aligned}$$

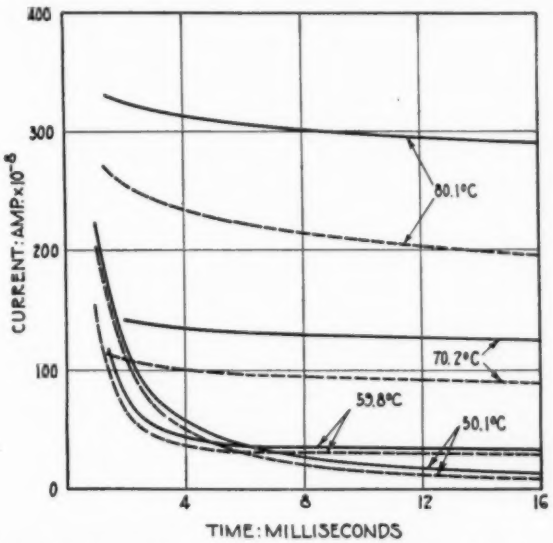


Fig. 2. Charge and discharge current-time relations at 1500 volts. Variation with temperature. Abietic acid specimen B12. Full line represents charge, broken line discharge.

A. C. Measurements

Fig. 3 shows the power factor temperature relation as measured for three different specimens of abietic acid having different programs of preparation and assembly. Sample B-9 the first to be tested was melted and cooled in the container several times before the measurements and was subjected to 135°C over a total time of several days. Difficulty in repeating readings in the high temperature range indicated changes due to temperature. B-11 was therefore taken from the same supply and heated only long enough for the complete filling of the test condenser. On reheating after the measurements indicated in curve B-11 of Fig. 3, it was found that close repetition of the first curve was possible only up to 55°, the values at higher temperatures all being higher than as first observed. Curve B-12 is the result of another series of values at decreasing temperature. These results indicate clearly a pronounced increase of conductivity at sustained high temperature with consequent irregularities of behavior in loss and power factor as related to temperature. For support of this conclusion we are indebted to the Electrical Testing Laboratories, New York, for a series of runs on samples of our material. They found pronounced differences in value and temperature, for maximum power factor, as related to shape and material of the electrodes, and in successive temperature cycles.

Computation of a. c. Behavior from d. c. Curves

The dielectric loss and the power factor under alternating potential may be computed to a high degree of accuracy from the charge and discharge curves in accordance with von Schweidler's method.[6,7] Assuming for simplicity a single exponential decay of the type $\phi(t) = C_0\beta e^{-\alpha t}$. von Schweidler's admittance under alternating potential of frequency f is of the form

$$\overline{Y} = \omega(B_r + i(C_0 + A_r)) \tag{2}$$

in which $\omega = 2\pi f$, C_0 = geometric capacitance of condenser with dielectric

$$A_r = C_0 \frac{\alpha\beta}{\omega^2 + \alpha^2}; \quad B_r = C_0 \frac{\omega\beta}{\omega^2 + \alpha^2}. \tag{3}$$

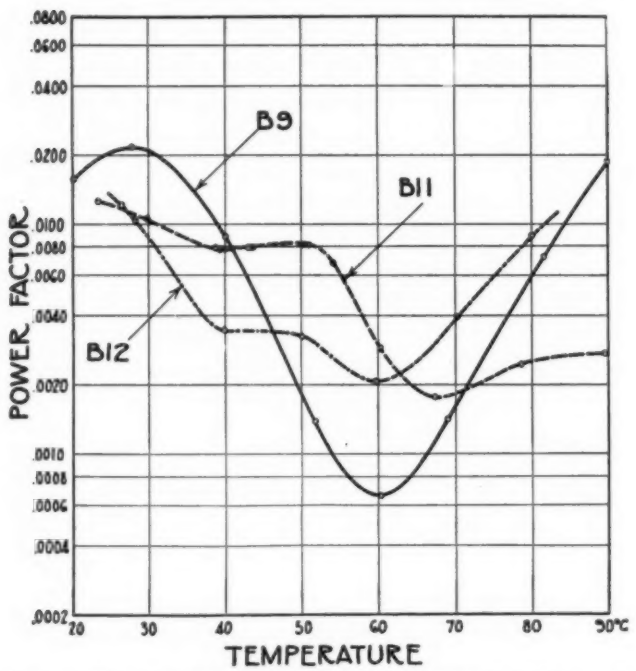


Fig. 3. Comparison of abietic acid specimens. Power factor-temperature curves at 1500 volts.

If, as in our case $\phi(t)$ consists of a series of terms we have:

$$\frac{A_r}{C_0} = \sum_1^n \frac{\alpha_n\beta_n}{\omega^2 + \alpha_n^2}; \quad \frac{B_r}{C_0} = \sum_1^n \frac{\omega\beta_n}{\omega^2 + \alpha_n^2} \tag{3'}$$

values which may be computed directly therefore from Eqs. (1). Using these values and formula (2) the power factor may be computed from the d.c. measurements and compared with the value as measured on the Schering bridge. This gives the loss due to reversible absorption. That due to irreversible conduction is computed from the generally constant difference between the

[6] von Schweidler, Ann. d. Physik **24**, 711 (1907).

[7] Whitehead, Journal Franklin Institute **208**, 453 (1929).

charge and discharge curves. Table I shows a close agreement between the measured values of power factor and the total as computed from the curves of charge and discharge, for several points on curve B-12.

TABLE I. *Analysis of dielectric loss at 1500 volts, 60 cycles by computation from d.c. characteristics abietic acid specimen B12.*

	Measured at 60 ~			Computed from d.c. Characteristics							
				Reversible Absorption			Irreversible Conduction			Total	
Temp. °C	Charging Current amp. $\times 10^{-6}$	Power factor	Dielectric loss watts $\times 10^{-6}$	Equivalent constant current amp. $\times 10^{-6}$	Power factor	Loss watts $\times 10^{-6}$	Initial constant current amp. $\times 10^{-6}$	Power factor	Loss watts $\times 10^{-6}$	Power factor	Dielectric loss watts $\times 10^{-6}$
T	I	$\tan \psi$	W	I_r	$\tan \psi_r$	W_r	I_i	$\tan \psi_i$	W_i	$\tan \psi_s$	W_s
50.0	385	0.00322	1860	1.117	0.00290	1675	0.114	0.00030	170	0.00320	1845
59.7	386	0.00206	1195	0.713	0.00185	1070	0.088	0.00023	130	0.00208	1200
70.2	386	0.00392	2270	1.091	0.00283	1640	0.350	0.00091	525	0.00374	2165
80.0	388	0.00885	5160	2.637	0.00680	3960	0.800	0.00208	1200	0.00888	5160

It should be noted that the method of von Schweidler is completely general and shows how the phenomenon of residual charge in a dielectric obeying Curie's laws, may be utilized for predicting behavior under alternating potential, whatever be the nature of the underlying phenonenon causing the delayed or decaying discharge. Therefore while originally, and as developed by Wagner[8], it was applied to the theory of dielectric absorption or residual charge as developed by Maxwell, it may with equal reliability be applied to compute a.c. losses arising in the theory of polar molecules. Both theories and analyses take their start from decaying functions of time, polarization being due to residual or absorbed charge in the one case, and to the return of polar molecules to a random distribution in the other.

von Schweidler's expression for the alternating admittance is given in Eq. (2). In Debye's treatment the dielectric constant is considered complex and so the admittance is:

$$\overline{Y} = \omega C_a(\epsilon'' + i\epsilon') \tag{4}$$

in which C_a is the capacitance of the condenser with vacuum as dielectric. Equating real and imaginary terms respectively, noting that $\epsilon_0 = C_0/C_a$ is the optical dielectric constant, and that ϵ_1 is the "static" dielectric constant, i.e., the value of ϵ' when $\omega = 0$, there results the following relation between τ Debye's relaxation time, and $\tau_0 = 1/\alpha$ that of von Schweidler's treatment:

$$\tau_0 = \frac{\epsilon_1 + 2}{\epsilon_0 + 2}\tau. \tag{5}$$

The extension of either theory reveals a maximum of power factor at a temperature dependent on frequency and time constant, with associated change in dielectric constant, and for those materials in which ϵ_1 and ϵ_0 do not differ greatly, such as resin, or impregnated paper, $\tau = \tau_0$. This method of analysis alone, therefore, cannot be expected to distinguish between the two types of loss. However, the d.c. charge and discharge curves show variations with temperature which seem to permit a nearer view of the phenomena involved.

[8] Wagner, Arch. f. Elek. III B, 3 and 4, 1914.

Anomalous Relaxation Time of Rosin

In Debye's[9] treatment the relaxation time is given as $\tau = 8\eta a^3/2kT$ in which η is the viscosity coefficient, a the radius of the molecule, k is Boltzmann's constant, and T the absolute temperature. With increasing temperature η decreases, and so we should expect a continual decrease of relaxation time with increase of temperature. However, we have found a departure from this behavior in the case of abietic acid.

The relaxation time or the time within which the discharge current decays to $1/e$ of its initial value, may be computed from Eqs. (1). These values show a decrease of relaxation time from 50° to 60° increasing again to 70° and decreasing beyond this value. This behavior is also evident by inspection of the curves of Fig. 2. The values from Eqs. (1) involve extrapolation beyond the range of time within which the equations are derived, as the discharge records do not extend below 0.001 sec.; thus the values may be taken as approximate only. That this involves only the question of numerical value and not the type of behavior is shown by employing an "equivalent single exponential"

$$\phi_0(t) = C_0\beta_0 e^{-\alpha_0 t}$$

instead of the complete Eq. (1) such that

$$\frac{A_r}{C_0} = \frac{\alpha_0\beta_0}{\omega^2 + \alpha_0^2} = \sum_1^n \frac{\alpha_n\beta_n}{\omega^2 + \alpha_n^2}; \quad \frac{B_r}{C_0} = \frac{\omega\beta_0}{\omega^2 + \alpha_0^2} = \sum_1^n \frac{\omega\beta_n}{\omega^2 + \alpha_n^2}$$

that is, a single exponential giving at the frequency in question the same a.c. values as the more complex d.c. curves. Then we have:

$$\alpha_0 = \frac{A_r}{B_r}\omega; \text{ and } \beta_0 = \omega\frac{B_r}{C_0}\left\{1 + \left(\frac{A_r}{B_r}\right)^2\right\}.$$

Obviously the relaxation time of the equivalent single exponential is $1/\alpha_0$. Fig. 4 shows the variation in the relaxation time with temperature as computed from the discharge curves and also as based on the equivalent single exponentials. The agreement is quite close for the lower parts of the curves since the relaxation time is less than the time interval used for computing the Eqs. (1). Extrapolation beyond this interval is necessary for the upper values as computed from the curves; this results in undue prominence of the slowly decaying components of the complex discharge curve and so to too high values of relaxation time. The curve based on the equivalent single exponential gives a more accurate composite value. As seen the type of variation in either case is the same, and there is a region of sharp discontinuity in the time constant-temperature curve between 60° and 70°, in which the time constant rises rapidly with increasing temperature, reaches a maximum at 70° and then decreases steadily with further increase of temperature. Considering these facts from the standpoint of the theory of polar molecules, we note that at 60° two time constants are evident, their ratio being about 30. Assuming

[9] Debye, "Polar Molecules", Chemical Catalog Co., Inc., New York.

that the viscosity is changing uniformly this indicates using Debye's expression as above, for the time constant, that two particles are involved the ratio of their radii being about 1 to 3.

The abrupt change in relaxation time, shown in Fig. 4, is caused by the increase in the value of the discharge current of the material with increase in temperature, as indicated in Fig. 2. It will be noticed that at 50° the charge and discharge components are nearly coincident but that each decays relatively rapidly. With increasing temperature not only is there an increase of conductivity, represented by the difference between the charge and discharge curves, but the ordinates of each have increased greatly, indicating an increase of stored charge with increase of temperature and a very much slower rate of decay of the two curves. On analysis it is found that the curves are

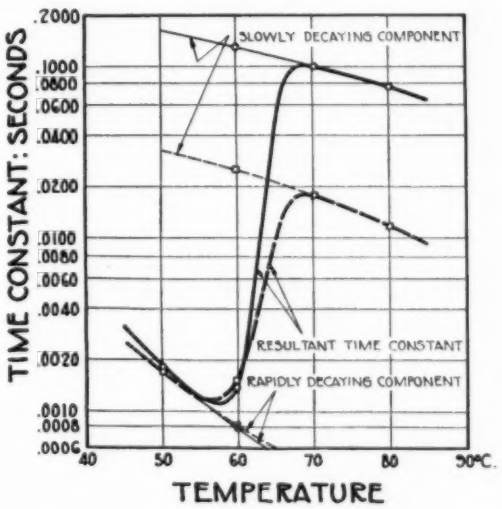


Fig. 4. Variation of time constant with temperature. Abietic acid specimen B12. Broken curves represent data computed from the equivalent single exponential as $\tau_0 = B_r/\omega A_r$. The full curves represent computed time constant: $\tau_0 = (t_2 - t_1)$, where $t_1 = 0.001$ and t_2 such that $i_1/i_2 = 2.7183$.

closely represented each by two components of the type βt^{-n} one rapidly decaying and the other slowly decaying. With increasing temperature the former falls rapidly in absolute value, becoming negligible in the neighborhood of 70°, at which point the slowly decaying component is rapidly increasing and makes its maximum contribution to the resultant time constant. It is also evident that with increasing temperature the time constant of the latter also falls off and the resulting power factor and loss partake ultimately more and more of the nature of conduction. The slowly decaying component, first measurable at 60°C, is increasingly predominant with rising temperature.

These two components of the discharge curve are both present in the temperature interval 50°–70° and make their separate contributions to the loss and power factor. A loss due to conduction alone also appears and increases rapidly with temperature. Table II shows the changing values of the

TABLE II. *Analysis of power factor at 1500 volts, 60°C. abietic acid specimen B-12.*

Time °C	Reversible Absorption Components			Irreversible conduction component	Total power factor
	Rapidly decaying	Slowly decaying	Total absorption		
50.0	0.00290	*	0.00290	0.00030	0.00320
59.7	0.00095	0.00095	0.00185	0.00023	0.00208
70.2	*	0.00283	0.00283	0.00091	0.00374
80.0	*	0.00680	0.00680	0.00208	0.00888

* Too small to detect.

contributions of each of these components to the total power factor in the temperature interval 50°–70°.

CHANGE OF DIELECTRIC CONSTANT WITH TEMPERATURE

Fig. 5 shows in the upper curve the variation of dielectric constant with temperature as computed from alternating current measurements of the capacitance. As seen the dielectric constant rises from 2.62 to 2.88 between 10°

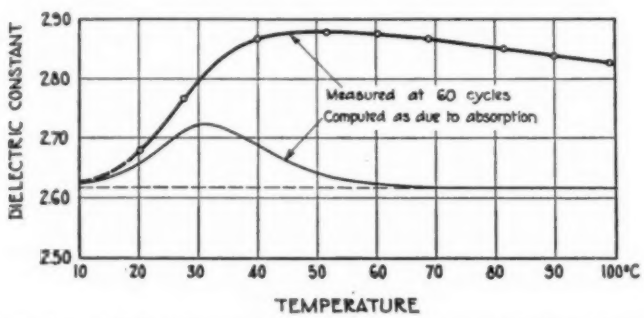


Fig. 5. Variation of dielectric constant with temperature. Abietic acid specimen B9.

and 50°, the maximum rate of increase occurring at about the same temperature as the maximum of power factor (Fig. 3). This is a well-known consequence of Debye's theory. It is apparently not so well known that a similar behavior is called for by von Schweidler's analysis of dielectric absorption under an alternating electric field. While the methods of analysis of the alternating case by von Schweidler and by Debye are slightly different, since the former uses the normal expression for the admittance, and the latter prefers to introduce a complex dielectric constant for expressing the total behavior, the two treatments are essentially the same. The result in each case is that the application of an alternating electromotive force to a dielectric showing an after polarization, as indicated by a decaying discharge curve, results in a dielectric loss and in an increased dielectric constant, which is inherent in the magnitude and in the equation of the variation of this discharge curve.

We have shown in this paper and elsewhere the close agreement between the measured and the computed values of power factor and loss using von Schweidler's method. When, however, we attempt to compute the increase in capacitance due to the relaxation function, we find the values given in the

lower curve of Fig. 5, which indicates an initial rise in the computed dielectric constant with increasing temperature, in accord with measured values, but thereafter a decreasing contribution and obvious discrepancy between measured value and that computed from the d.c. curves. The discrepancy is apparent only and due to the fact that the discharge curves as measured begin 0.001 sec. after the beginning of discharge. It so happens that with increasing temperature the rapidly decaying components of the curves shrink so far back into this interval that they may not be estimated properly from the curves as taken. Eqs. (3) show that these components (large values of α) do not contribute to B_r the loss component of the admittance, but may cause relatively much larger values of A_r than indicated from the curves as taken. It is evident that this experimental discrepancy is independent of the origin of the relaxation function. It is equally evident that alternating measurements of loss, power factor, and capacitance do not offer a promising means of distinguishing between the theories of polar molecular orientation and of dielectric absorption as explanations of the variations of these quantities with temperature and at low alternating frequencies.

Discussion

Referring to Fig. 4 and the suggestion that the two curves of relaxation times indicate two types of polar particle, it appears more likely that the slower type, at least, is due to conduction. Whitehead and Marvin[10] have reported similar types of slow charge and discharge in insulating oils which were clearly associated with a volume distribution of space charge, and due to some type of large slow moving ion or charged colloid particle. There is some difficulty in this view for resin owing to its high viscosity, but on the other hand the time constant is extremely short as compared with those found in the lighter oils, indicating a rapid initial but restricted motion as limited by the viscosity. Further, the component of loss and power factor due to this slow component of time constant increases rapidly with increasing temperature, following the behavior of oils, in which it finally merges into a loss due to simple conduction.

As to the rapidly decaying component, viewed from the standpoint of Debye's theory, it is difficult to picture a distribution of kinetic molecular activity which would be subject to influence by the relatively slow period of a 60 cycle field. Either abnormally high values of viscosity are necessary, or dimensions greater than molecular must be attributed to the polarized particle. There is, on the other hand, much evidence in favor of anomalous conduction and absorption as an explanation. For example, we have also observed the rapid charge and discharge curves which account for power factor, in high grade relatively light insulating oils, which are commonly supposed to be free from polar substances. The work of Gement and Borman,[3] mentioned above, shows that similar power factor maxima may be obtained by the admixture to oils of non-polar impurities. The differences among the shapes of our successive power factor curves (Fig. 3) strongly suggest differ-

[10] Whitehead and Marvin, Trans. A.I.E.E. **49**, April (1930).

ences in structure, following successive temperature cycles, and changes in the relation of conducting to solid portions of the material. From this point of view, the rising power factor in passing from high to low temperature would be accounted for somewhat as follows: At high temperature the power factor is entirely accounted for by conduction. With decreasing temperature we first have a separation of space charges due to restricted conduction and a resulting polarization. With irregular solidification there is a combination of conducting channels and fissures with non-conducting solid portions resulting in a typical dielectric absorption. The chief evidences of this are the change in the maximum of power factor both as regards value and the temperature at which it occurs, resulting from initial changes in conductivity on successive temperature cycles.

Acknowledgments

This work is part of a research supported by the Utilities Research Commission of Illinois, for which grateful acknowledgment is hereby made. Cordial thanks are also extended to Dr. S. K. Waldorf and Mr. A. Baños, Jr., for their skilful conduct of the experiments and computations.

Conclusions

(1) The power factor, dielectric loss, and capacitance at 60 cycles of abietic acid have been measured over the temperature range 20° to 100°.

(2) A maximum of power factor is found at about 30° and a minimum at about 60°. Under repeated temperature cycles with change of sample and with different materials of electrodes, the power factor maxima and minima change as to value and temperature.

(3) With increasing temperature the dielectric constant rises from about 2.6 to 2.8 within the temperature interval 20° to 50°, the maximum rate of rise being at about 30°.

(4) Short time charge and discharge curves with the amplifier oscillograph have permitted the direct measurement of the relaxation time over the same temperature range. It is shown in general that there are two principal components of the discharge curve which lead to two types of relaxation time, one being the principal factor in the dielectric loss at low temperatures, and the other at high temperatures. The value at 55° is about 0.0012 sec., and at 70° about 0.018 sec.

(5) The discharge curves have been used for an analysis of the alternating current behavior following the method of von Schweidler. There is uniform agreement between measured and computed values of loss.

(6) The results are discussed in the light of dielectric absorption in the Maxwell sense and of Debye's theory of polar molecules. The conclusion is reached that alternating current measurements at 60 cycles of power factor, loss, and capacitance do not offer a promising method of distinguishing between the two theories, since the same behavior is predicted by each.

HEAT WAVES THROUGH INSULATING WALLS

By Emerson M. Pugh and F. C. Houghten
Carnegie Institute of Technology and Research Laboratory of American Society of Heating and Ventilating Engineers and Pittsburgh Station of the U. S. Bureau of Mines

(Received December 31, 1931)

Abstract

For calculating the flow of heat through walls of buildings the steady state formula based upon average temperatures has been found inadequate. A solution for the periodic heat flow through such walls is given, which has been simplified so that it depends upon two dimensionless quantities f and βl, which are functions of the physical properties of the walls and the periodicity. Curves are given which make it possible to read off the solution directly as soon as f and βl are known. An experimental check is given.

IN DESIGNING heating and air conditioning systems for buildings, the engineer has calculated heat transfer through the walls from coefficients determined under steady state conditions. For such calculations, it was assumed that the average inside and outside temperatures remained constant. These assumptions have proven sufficiently accurate for practical purposes in designing for winter conditions, but it has been recognized that they do not hold when applied to the cooling and air conditioning of buildings for human comfort in summer, where more exact engineering is required, and where the diurnal cyclic change in the outside surface temperature of the structure has a much greater amplitude.

For the cyclic changes in temperature experienced in the summer, the rate of heat transfer through the interior surface of the wall may vary over wide limits, the direction of heat flow may be reversed during the twenty-four hour period, and the time of maximum heat penetration through the inner surface may lag several hours beyond the crest of the temperature wave on the outside surface. For this condition, the instantaneous rate of heat flow through the inner surface depends upon the outside surface temperature, the conductivity, the heat capacity, the density, the thickness of the wall, and the heat transfer coefficient for the inside surface.

The following solution, the application of which has been verified by experiments carried on by the Research Laboratory of the American Society of Heating and Ventilating Engineers, in cooperation with the Pittsburgh Station of the United States Bureau of Mines, and Carnegie Institute of Technology, has been put in such form to make the numerical calculations simple.

The solution should be of interest not only to the heating and ventilating engineer, but also to others interested in maintaining a constant temperature in any medium or space. A thermostat does not keep the temperature absolutely constant, but keeps it oscillating about the desired temperature, with

more or less definite frequency and amplitude. If the space or medium, the temperature of which is to be maintained constant, is placed within a box with walls of low diffusivity, and if the space surrounding the box is controlled by a thermostat, the amplitude of the temperature oscillations within the box may be made a small fraction of that in the thermostatically controlled space outside.[1]

In its simplest form, the problem is to evaluate the heat flow through the inner surface of a homogeneous slab, having given, the temperature cycle of the outside surface, the constant temperature at which the inside atmosphere is maintained, and the physical constants of the slab.

Mathematically, we wish to obtain the solution of the equation of heat flow

$$\frac{\partial \theta}{\partial t} = h^2 \frac{\partial^2 \theta}{\partial x^2} \tag{1}$$

which will satisfy the boundary conditions

$$\theta = \theta_0 \sin \omega t \text{ at } x = 0 \tag{2}$$

and

$$k \frac{\partial \theta}{\partial x} + \epsilon \theta = 0 \text{ at } x = l. \tag{3}$$

We are assuming for the sake of simplicity, that the average temperature over a complete cycle is zero on both sides of the slab. No generality is lost by this assumption, for when the average temperatures on either side of the slab differ from zero, we may calculate the steady flow of heat due to these average temperatures and add the two solutions.

For solving the oscillatory case, we will define our terms as follows: k = coefficient of thermal conductivity of slab; ρ = density of slab; c = specific heat of slab; ϵ = ratio of the heat flow per unit area from the slab surface to the air, to the difference in temperature between this surface and air, assumed constant; l = thickness of the slab; $\omega = 2\pi/T$ where T is the period of the temperature oscillations; $h = (k/c\rho)^{1/2}$; $\beta = 1/h(\omega/2)^{1/2} = (c\rho\omega/2k)^{1/2}$; $f = \epsilon/k\beta = (2)^{1/2}/(c\rho\omega k)^{1/2}$. The solution is

$$\theta = c_1 e^{-\beta x} \sin (\omega t + \gamma_1 - \beta x) + c_2 e^{\beta(x-2l)} \sin \{\omega t + \gamma_2 + \beta(x - 2l)\}. \tag{4}$$

According to George Green,[2] the first term would represent the direct wave, and the second term a wave reflected from the inner surface. In the general case, there may be multiple reflections as in the optical case, and so each term must represent the sum of an infinite series of waves.

It will be convenient to write (4) in the following form:

$$\theta = \frac{\theta_0}{B} e^{-\beta x} \sin (\omega t + \alpha - \beta x) + \frac{A\theta_0}{B} e^{\beta(x-2l)} \sin \{\omega t + \alpha + \sigma + \beta(x - 2l)\} \tag{5}$$

[1] Thermostat Design for Frequency Standards, by W. A. Marrison, Bell Telephone Journal, August, 1928.

[2] London, Edinburgh and Dublin Philosophical Magazine, Page 784, April, 1927.

where

$$A = \left(\frac{(1-f)^2+1}{(1+f)^2+1}\right)^{1/2}$$

$$\sigma = \cos^{-1}\frac{2-f^2}{(4+f^2)^{1/2}} \text{ where } 0 \leqq \sigma \leqq \pi$$

$$\alpha = \sin\frac{A}{B}e^{-2\beta l}\sin(\sigma - 2\beta l) \text{ where } -\pi < \alpha < \pi$$

$$B = (1 + A^2e^{-\beta l} + 2Ae^{-\beta l}\cos(\sigma - 2\beta l))^{1/2}.$$

In practice, $e^{-2\beta l}$ will be small, and $e^{-4\beta l}$ will be very small, while A must lie between 0.546 and +1.00. Therefore, $B=1+Ae^{-2\beta l}\cos(\sigma-2\beta l)$ approximately, which shows that we may set $B=1$ and $\alpha=0$, and the resulting solution

$$\frac{\theta}{\theta_0} = e^{-\beta x}\sin(\omega t - \beta x) + Ae^{\beta(x-2l)}\sin\{\omega t + \sigma + \beta(x-2l)\}$$

will not be in error by more than $e^{-2\beta l}$ in unity.

We are only interested in the temperature of and the heat flow from the inner surface of the slab where $x=l$.

Here

$$\frac{\theta}{\theta_0} = \frac{\theta_i}{\theta_0} = e^{-\beta l}\{\sin(\omega t - \beta l) + A\sin(\omega t - \beta l + \sigma)\}$$

which obviously represents a simple sine function of amplitude $Re^{-\beta l}$ where

$$R = (1 + A^2 + 2A\cos\sigma)^{1/2}.$$

$Re^{-\beta l}=\theta_m/\theta_0$ is the ratio of the amplitudes of the temperature variations on the inside of the wall to that on the outside. Since A and σ are functions of the single variable f, R is also a function of f, and may be plotted as in Fig. 1. For the purpose of quick computation, values of $e^{-\beta l}$ have been plotted in Fig. 2 against βl.

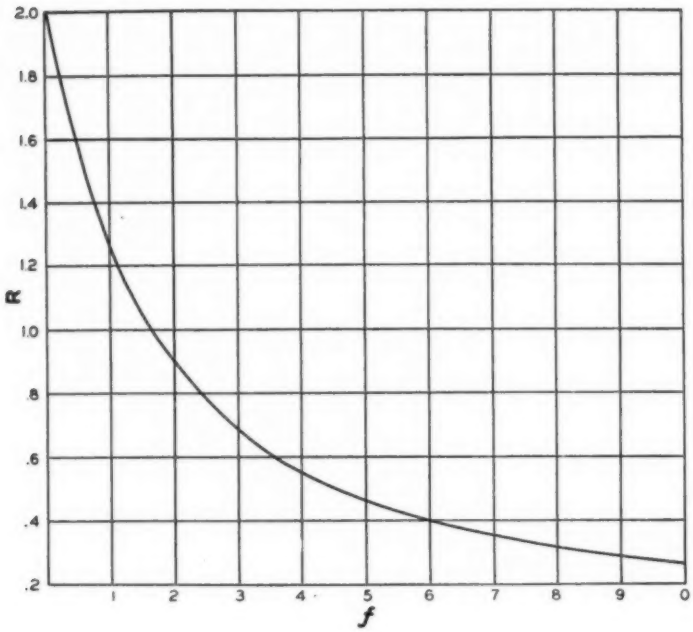
To find the value of θ_m/θ_0 it is only necessary to calculate f and βl from the constants of the slab, and take the product $Re^{-\beta b}$ from Fig. 1 and Fig. 2. Both f and βl are dimensionless and so may be calculated in any self-consistent system of units, which is a distinct advantage for engineering purposes.

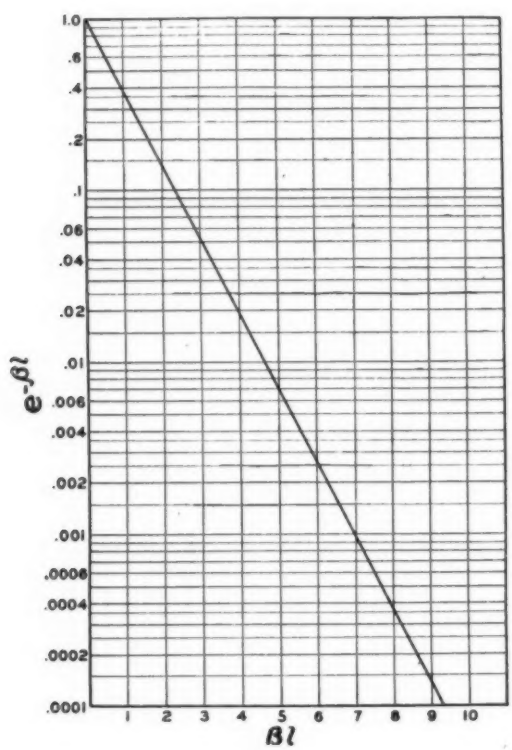
The temperature at the inner surface may now be expressed by the equation

$$\theta_i = \theta_m \sin\omega(t + t_0)$$

where t_0 is the time between the occurrence of the temperature maxima at the outside and inside surfaces. The temperature is maximum at the outside surface when $\omega t=\pi/2$, and the corresponding maximum at the inside surface occurs when $\tan(\omega t-\beta l)=1+A\cos\sigma/A\sin\sigma$ where $(\omega t-\beta l)$ is in the first quadrant. Then

$$\omega t_0 = \left\{\tan^{-1}\left(\frac{1+A\cos\sigma}{A\sin\sigma}\right) - \frac{\pi}{2}\right\} + \beta l$$





Figs. 1 and 2.—Curves for calculating the ratio of the amplitude of the temperature oscillation on the outside wall surface to that on the inside.

is the phase angle between the inside and outside sinusoidal temperature waves. The bracketed terms can be plotted against f as in Fig. 3. *Thus, if the equation of the outside surface temperature is known, the equation of the inside*

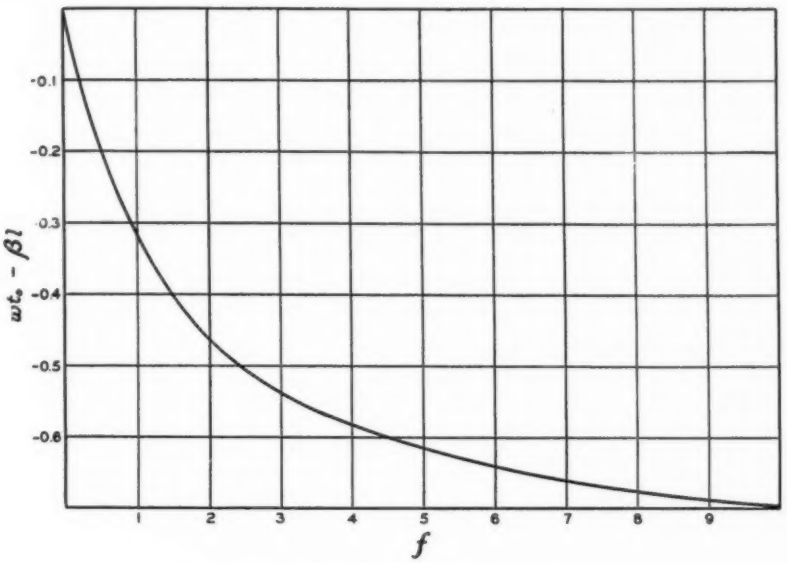


Fig. 3—Curve for calculating the time, t_0, required for the temperature maximum to travel through the wall.

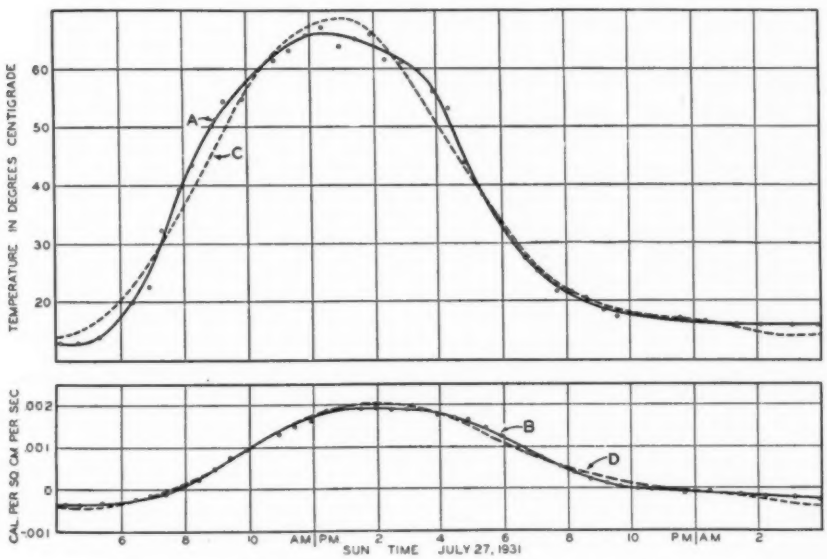


Fig. 4. Heat flow through 2″ pine slab due to solar radiation. Curve A is the upper surface temperature, and curve B is the heat flow from the lower surface, both determined by experiment. Curve D is the heat flow from the lower surface predicted by the theory from the Fourier analysis C of curve A, using only two terms.

surface can be obtained directly from Figs. 1, 2, and 3 after f and βl have been calculated. The heat flow is simply $\epsilon\theta$.

At the Research Laboratory of the American Society of Heating and Ventilating Engineers, an extensive study was made of the way in which heat from the sun travels through slabs of different materials. Roof slabs of the desired material, equipped with Nicholls heat flow meters[3] and thermocouples on the upper and lower surfaces, were exposed to solar radiation and prevailing outside temperatures above, and to conditioned air below. The results of this experimental study have been checked against the predictions of this theory. The equation of the outside temperature of the slab has been obtained by Fourier's series, only two terms being needed to obtain the desired accuracy. Fig. 4 shows a typical check on a 2-inch pine slab. Curve A is the upper surface temperature, and curve B is the lower surface heat flow, both determined by experiment, while curve D is the inside heat flow predicted by the theory from curve C which is plotted from the first two terms of the Fourier analysis of curve A. It is not surprising that the calculated heat flow from the inner surface D, fits the actual heat flow B, better than the Fourier curve C, from which it was calculated, fits the outside temperature curve A, because the higher harmonics which are neglected by C are damped out more rapidly than the lower frequencies on passing through the slab, since the damping factor β is proportional to the square root of the frequency.

[3] Measuring Heat Transmission in Building Structures and A Transmission Meter, by P. Nicholls. Page 65, Transactions Amer. Soc. of Heat. and Vent. Engrs., 1924.

EDITOR'S COLUMN

The Excitation of Atomic Mercury by Election Impact

IN A recent paper in the Physical Review, Dr. W. Penney[1] has given a computation of the probability of excitation of the four P levels of the mercury atom by electron impact. One of these levels is a singlet like the normal state, while the others form the components of a triplet state ($2\,^3P_{0,1,2}$). The transition from the middle component ($2\,^3P_1$) to the normal state ($1\,^1S_0$) gives rise to the resonance line 2537A.

The procedure used in determining the probability of excitation is to calculate the "cross-sectional area for the transition" which is a kind of average target area of the atom such that the probability that the given excitation process will occur is given numerically by this cross-sectional area. There is a particular cross-sectional area to be assigned to each kind of collision. An approximate formula for this target area of the atom has been calculated by Dirac[2] and by Born,[3] who have based their derivations on somewhat different theories to be sure, but leading to essentially identical results.

In order to calculate the terms appearing in these formulae for the scattering area for the excitation processes one must have wave functions for the different states of the mercury atom, even if only approximately. Penney has obtained these wave functions by an approximate method based upon Slater's work on complex spectra.[4] It is the determination of these functions which gives the greatest trouble and introduces the greatest uncertainties in the final result.

The calculations show that the probabilities of excitation of the triplet levels by electron impact increase rapidly for electron velocities above the excitation potentials for the various terms to maxima in the neighborhood of 6∼7 volts and then decrease somewhat more slowly. For the $2\,^3P_0$ and $2\,^3P_1$ levels the cross-sectional areas drop to zero in the region 20∼25 volts, but for the $2\,^3P_1$ level the cross-sectional area seems to approach asymptotically a small finite value. This is in contrast to previous work of Massey and Mohr[5] whose calculations on the similar transitions in the helium atom indicated that the excitation probabilities for the triplet levels should all vanish with increasing electron velocity.

For the excitation of the $2\,^1P_1$ level, on the other hand, the calculated cross-sectional area rises to a high maximum in the region 18∼20 volts and then decreases rather slowly, being much larger that the corresponding areas for any of the triplet levels. These results seem to be in generally good agreement with the experimental facts wherever the latter are available, insofar as values for the relative excitation probabilities for the different transitions are considered. The calculated absolute excitation probabilities are too high by a factor of two, which is undoubtedly a result of the difficulty of obtaining sufficiently accurate wave functions which are yet not too clumsy for computational purposes.

E. L. HILL

[1] W. G. Penney, Phys. Rev. **39,** 467 (1932).

[2] P. A. M. Dirac, Quantum Mechanics, Oxford, 1930, Chapter X.

[3] M. Born, Zeits. f. Physik **38,** 803 (1926).

[4] J. C. Slater, Phys. Rev. **32,** 349 (1928).

[5] H. S. W. Massey and C. B. O. Mohr, Proc. Roy. Soc. **A132,** 605 (1931).

The Dissociation of Molecules by Electron Impact

IN THE early days of the quantum theory of the atom, when Bohr's methods were on the threshold of their long series of successful applications, the experiments on the controlled bombardment of atoms by electrons so successfully prosecuted by Franck and Hertz[1] and later extended by numerous other work-

[1] J. Franck and G. Hertz, Verh. der Phys. Ges. **16,** 10 (1914).

J. Franck and P. Jordan, "Anregung von Quantensprüngen durch Stösse," Berlin 1926.

K. T. Compton and F. L. Mohler, "Critical Potentials", Nat. Res. Council Bulletin No. 48, Washington, D. C. 1924.

ers, provided most substantial support for the theory. The evidence obtained in this way on the correctness of the interpretation of the spectroscopic term values as energy levels was an important factor in establishing confidence in the quantum theory.

While experiments on the excitation of atoms by electron bombardment have been extensively performed and have yielded results of great importance in the study of atomic structure, the extension to diatomic and more complicated molecular systems has not been carried out in such detail. This is certainly because of the complications attending the interpretation of such experiments.[2]

In recent numbers of the Physical Review a series of papers has appeared describing the results of work done in the Physical Laboratory of the University of Minnesota by Professor J. T. Tate and his co-workers[3] on the dissociation of molecules by electron impact. In most of these experiments some of the more common diatomic molecules have been studied (H_2, N_2, O_2, CO, and NO), but some work has also been done on H_2O (water vapor) and C_2H_2 (acetylene).

For even the simplest of diatomic molecules, H_2, the number of things which can happen in a collision with an electron is much greater than in the collision of an electron with an atom. The first and most striking result of these experiments was the discovery that the dissociation which takes place through the effect of the collision must occur with considerable violence since ions are observed which possess energies ranging from 2 to 8 volts and in numbers far exceeding those having energies in this range due to the ordinary thermal agitation. Apparently the electron does something to the molecule which causes the latter literally to explode.

The explanation of the phenomenon from the point of view of quantum mechanics was at once given by Condon,[4] and has since been very useful in the interpretation of the experimental data. One can consider the motion of a diatomic molecule, apart from its translational motion as a whole—its "kinetic theory" motion—as composed first of the extremely rapid motions of the electrons about the nuclei, these motions being practically independent of the slower motions of the nuclei so that the electrons occupy quantized orbits, second the vibration of the nuclei along their line of centers under the influence of a law of force which is dependent upon the configurations of the electrons, and lastly the rotational motion of the molecule as a whole. When the molecule collides with a fast electron the primary interaction takes place between the impinging electron and the electrons in the molecule, an interaction which in general will lead to an electron jump (transition) of the molecular electrons from one orbit to another. The principal result of this change of electronic state is that the law of force which governs the vibrations of the nuclei changes also, and it may occur, according to quantum mechanics, that the new law of force between the nuclei is such that the two parts of the molecule repel rather than attract each other. This change of state of the electrons takes place very rapidly compared to the relatively slow oscillations of the nuclei so that after it has occurred the two atoms are left very close together but repelling each other vigorously, the result being that they fly apart with considerable velocities. The energy which is available for transfer into kinetic energy in this manner depends upon the amount of energy which has been given up to the molecule by the impinging electron and on the character of the repulsive energy state. This excess energy is then divided between the two decomposition products in such a way as to satisfy the equations for the conservation of energy and linear momentum. This corresponds precisely to the observations which even verify the theoretical distribution of energy between the two atoms. The experiments can thus be considered as an important substantiation of the existence of repulsive energy states in molecules, and so of the correctness of the quantum mechanical approach to the problem of molecular structure.

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[2] See H. D. Smyth, Rev. Mod. Phys. **3**, 347 (1931) for a review of the field.

[3] W. Bleakney and J. T. Tate, Phys. Rev. **35**, 658 (1930).

W. Bleakney, Phys. Rev. **35**, 1180 (1930).

W. W. Lozier, Phys. Rev. **36**, 1285 (1930).

A. L. Vaughan, Phys. Rev. **38**, 1687 (1931).

J. T. Tate and W. W. Lozier, Phys. Rev. **39**, 254 (1932).

J. T. Tate and P. T. Smith, Phys. Rev. **39**, 270 (1932).

[4] E. U. Condon, Phys. Rev. **35**, 658 (1930).

In the recent work of Tate and Lozier[5] the dissociation products from N_2 and CO have been studied. Among the most interesting results to which the experiments lead (in conjunction with the mass spectrograph measurements of Vaughan)[3] are estimates of the heats of dissociation of the molecules. The heat of dissociation of $N_2 \rightarrow N+N$ is set at 8.4 (electron) volts which is about 0.7 volt below the value estimated previously by Birge, while a lower limit of 7.1 volts is set for the heat of dissociation for the reaction $N_2^+ \rightarrow N^+ + N$. In CO the energy absorbed in the dissociation $CO \rightarrow C+O$ is found to be 9.3 volts. The values are extrapolated in such a manner as to give the heats of dissociation for an adiabatic separation of the two decompositions products in which they are left finally with no kinetic energy.

Tate and Smith[6] have measured the ionization potentials and the efficiencies of ionization for a number of molecules, and give the following values N_2 (15.7); CO (14.1); NO (9.5); H_2 (15.6); C_2H_2 (11.6) and O_2 (12.5 and 16.1), the numbers in parentheses giving the values of the observed ionization potentials in volts.

Lastly we may mention an interesting circumstance which has been observed in these experiments (as well as in some of the earlier work of Lozier[3] and Vaughan[3]); namely, the appearance of negative ions. For example, in the dissociation of CO it has been found that O^- ions are present in quite appreciable amounts. If one studies their formation as a function of the energy of the bombarding electrons he finds that up to about 10 volts only small numbers of the ions are formed, while between 10 and 14 volts quite a considerable number is formed. Electrons with energies in the neighborhood of 11 volts seem very efficient in their formation, but when the electron energy goes above 14 volts then the efficiency drops to a small value (perhaps even to zero), to rise again monotonically when the energy exceeds 22 volts. The narrowness of the range of energies around 11 volts within which the impacting electrons are efficient in producing O^- ions from CO leads to the supposition that the process may be one of attachment of the electron to the neutral CO molecule followed by a dissociation of the molecular ion. The exact way in which this takes place is not clear.

While this work is certainly only in its inception, and will probably yield much valuable information about the structure of molecules as the field becomes explored its evidence on the existence of real repulsive energy levels for molecules is especially opportune as another pillar of support for the quantum theory of molecules.

E. L. HILL

[5] J. T. Tate and W. W. Lozier, Phys. Rev. **39**, 254 (1932).

[6] J. T. Tate and P. T. Smith, Phys. Rev. **39**, 270 (1932).

The Quantum Theory of Radiation

WE HAVE previously noted in these columns[1] certain phases of the recent theoretical work on the nature of electromagnetic radiation, so that it seems quite appropriate to call attention to a paper by Professor E. Fermi of Rome, Italy, on this subject in the January 1932 issue of the Reviews of Modern Physics. This is the more appropriate since this article, which represents lectures delivered at the University of Michigan by Professor Fermi during the summer term of 1930, is the most extensive general summary of this field which has yet appeared in English.

The quantum theory of radiation in its present form was developed by Dirac in England, and has since been extended by numerous physicists, among whom Professor Fermi himself has been one of the most active. The first part of the paper gives a connected account of Dirac's theory as it leads to the quantization of the radiation field within an enclosure (Hohlraum) and its application to the explanation of various phenomena such as the broadening of spectral lines, the theory of Lippman fringes, the Doppler effect, and even the propogation of light. These topics bring out the power of the theory to give a consistent picture of phenomena some of which seem to be due to the peculiarly *wave* characteristics of light, while others seem to be

[1] Editor's Column, Physics **1**, 208 (1931); **2**, 60 (1932)

due to the special *quantum* properties of light.

In the second and third parts of his paper, Professor Fermi has given an account of the relation of this theory of radiation to Dirac's relativistic wave equation for the electron, and finally a short account of the quantum theory of electrodynamics. The problems here are numerous and by no means clear, so that we shall say no more about them.

In a current issue of the Physical Review, Professor Kennard of Cornell University presents a detailed theory of the radiation field along somewhat different lines.[2] Instead of representing the radiation as though it were enclosed in a finite volume so that it can be resolved into a Fourier series corresponding to a superposition of independent standing wave systems, the field is here represented by a Fourier integral made up of a continuous sequence of travelling waves. In order to carry through the comparison with the classical wave theory so far as it is possible, Professor Kennard bases much of his argument upon the method of wave packets. This increases the calculations appreciably, and makes the argument rather difficult to follow. Much of the beauty and simplicity of the method of Dirac, which is discussed in the paper of Professor Fermi, seems to be associated with the fact that it deals directly with the idea of probability—a calculation on this theory being ordinarily a determination of the probability that a certain event will occur, the character of the event to be specified beforehand—while the wave packet method deals with a superposition of a lot of possible events which may occur. In this method the electron is represented by a group of waves concentrated within a certain region which can be adjusted somewhat at pleasure to represent the fact that the electron is to be found within this region. According to present wave mechanical ideas this packet then also represents the unavoidable fact that the velocity of the electron is not specified with any great accuracy. The problem then is to calculate the interaction between the electromagnetic waves of the radiation field and the matter waves of the packet. The result of this interaction will be a change in the velocity and in general also a change in form of the packet. We can also interpret this procedure by saying that it represents the interaction of the radiation with a group of electrons, not affecting each other, but being acted upon in different manners by the field because they possess velocities and positions distributed over a certain range; i.e., the wave packet represents a group of electrons located within its boundaries but not all having the same velocity. In this way one can make a comparison of the results of the theory with the ordinary electromagnetic theory. For example if the geometrical size of the packet is made very large so that the position of the electron is quite indeterminate, but the velocity is correspondingly accurately known, then the presence of the radiation causes a very rapid spreading of the packet which can be interpreted in terms of a recoil of the electron. For a more detailed consideration of this and other points the reader must be referred to the original paper.

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[2] E. H. Kennard, Phys. Rev. **39**, 435 (1932).